Preparation and Characterization of Inorganic Membranes by using Sol-Gel Techniques

By

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A Dissertation Submitted to the Graduate School in Partial Fulfillment of the Requirements for the Degree of

MASTER OF SCIENCE

Department: Materials Science and Engineering Major: Materials Science and Engineering

> İzmir Institute of Technology İzmir, Turkey

> > April, 2000

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ACKNOWLEDGEMENTS

I would like to thank and express my deepest gratitute to Prof Dr. Muhsin Çiftçioğlu for his help, guidance, understanding and encouragement during this study and the preparation of this thesis.

I am very greatful to Prof. Dr. Masaharu Komiyama for his help, guidance and contribution during my AFM research in Yamanashi University, Japan.

I also would like to thank to Assist. Prof Dr. Fehime Özkan for her valuable comments and suggestions.

Special thanks are to all resarch assistants and laboratory technicians who helped me during the experimental work, for their friendship.

Finally I would like to thank my family for their help, support, patience and encouragement.

ABSTRACT

In this research the preparation of ceramic membranes for gas separation applications by using sol-gel techniques were investigated. The effects of water/alkoxide ratio, H⁺/alkoxide ratio on the catalysis of the hydrolysis-condensation reactions and the peptization process were investigated by using N₂ adsorptiondesorption isotherms, thermogravimetric analysis and FTIR (Fourier Transform Infra Red). The performance and the potential use of these materials in gas separation applications depend mainly on the ability in controlling-designing the microstructurepore network in these materials.

The alumina and silica sols were prepared by using aluminium isopropoxide and tetraethylorthosilicate. Sols with different H⁺ / Al⁺³ and H₂O / Al⁺³ ratios were prepared. These peptized clear boehmite sols were used for the preparation of unsupported Al₂O₃ membranes at 600 $^{\circ}$ C. The similar ratios were varied for the preparation of clear silica sols and these sols were further dried and heat treated at 400 $^{\circ}$ C.

The thermogravimetric analysis has shown that the weights of the unsupported membranes were stable at the above temperatures. The boehmite was observed to decompose to the γ -Al₂O₃ phase at about 425 ^oC. The FTIR analysis have proved the formation of boehmite in the sols and all the organic solvent peaks disappeared upon heat treatment.

The γ -Al₂O₃ membranes all displayed Type IV isothems typical of mesoporous materials. Hysteresis loops were present in all these isotherms and fast desorption took place in the 0.4-0.6 P/Po range. The BJH pore size distributions were sharp for all the samples.

The desorption pore size distributions were found to become wider at an intermediate acid content membrane which also had the lowest BET surface area. The BET particle sizes of these membranes were estimated to be in the 70-100 A^o range. The throat and pore cavity sizes of monosize sphere packings for this particle size range were observed to be in close agreement with the experimentally determined adsorption-desorption pore sizes.

The silica samples all displayed Type I isotherms with no hysteresis typical of microporous materials. The HK (Horvoath Kawazoe) pore sizes were in the 4-5 A^o range. An effect of the water content of these acid-catalyzed sols on the pore size were also detected.

Bu çalışmada gaz ayırma uygulamalarında kullanılabilecek seramik membranların sol-gel yöntemleriyle hazırlanması incelenmiştir. Su/alkoksit ve H⁺/alkoksit oranlarının katalizlenen hidroliz - yoğunlaşma reaksiyonları ve peptizasyon işlemlerine etkileri azot adsorpsiyondesorpsiyon izotermleri, termal analiz ve FTIR spektroskopisi kulllanılarak incelendi. Bu malzemelerin gaz ayırma ugulamalarındaki performans ve potensiyel kullanımları , gözenek ağlarının- micro yapısının kontrolü-tasarmına bağlıdır.

Alumina ve silika solları sırasıyla Aluminyum isopropoksit ve Tetraethylortosilikat kullanılarak hazırlanmıştır. Bu sollar değişik Su/ Al⁺³ ve Acid/Al⁺³ oranlarında hazırlanmıştır. Hazırlanan berrak Boehmite solları kullanılarak 600 °C de desteksiz membranlar hazırlanmıştır. Benzer oranlar değistirilerek berrak silica solları elde edilmiş ve bu sollar kurutulup 400 °C de ısıl işlemden geçirilerek desteksiz silika membranları üretilmişdir.

Termogravimetrik analiz sonuçları desteksiz membranlardaki kütle kaybının yukarıdaki sıcaklıklarda durağan hale geldiğini ve Boehmite'ın γ -Al₂O₃ Alumina fazına 425 °C de bozunduğunu göstermiştir. FTIR analiz sonuçları bütün sollarda boehmite oluştuğunu ve organik solvent piklerinin ısıl işlem sonrası kaybolduğunu göstermiştir.

 γ -Al₂O₃ membranlarında mezagözenekli malzemelerde görülen tipik Tip IV izotermleri elde edilmiştir. Bütün izotermlerde hysterisis loop göstermiştir ve hızlı desopsiyon 0.4-0.6 P/Po aralığında gerçekleşmiştir. Bütün alumina membranların BJH boşluk dağılım garafikleri belirgin pikler vermiştir. Desorpsiyon gözenek dağılımı 3 nolu asit içeriği olan membranda, ki bu en düsük yüzey alanına sahiptir, daha geniş bulunmuştur. Bu membranların BET parçacık büyüklüğü 70-100 A^o aralığındadır. Tek boyutlu bir küreler paketinde boğaz ve boşluk boyutları; hesaplanan parça büyüklük aralığı için, adsopsiyon-desorpsiyon gözenek boyutları ile uyum halindedir.

Bütün silika örnekleri için mikro malzemelerde görülen hysterisis loopu olmayan sollardaki Tip I izotermleri elde edildi. Harvoth-Kawazoe boşluk dağılımının 4-5 A^o aralığında olduğu ve sollardaki su içeriğinin boşluk dağılımına etkileri olduğu gözlenmiştir.

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CHAPTER 1

INTRODUCTION

Historically, the aim of mankind has been the separation and recombination of materials and matter. Along the BC period, during the cupper, bronze, and iron ages man tried to separate and process metallic materials. Nuclear research in atomic separations started the Atomic Age. Current work on separation of molecules and atoms in various high technology applications will determine the nature of civilization and the quality of life in the 21 st century.

Many manufacturing industries are based on separation processes. So far more efficient manufacturing better separation techniques will be needed in the future. New technologies try to develop new novel products. These separation technologies along with the primary factors affecting the separation are schematically shown in Figure 1.1 in relation with the sizes of the species to be separated.





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Many conventional techniques such as distillation, extraction, centrifugation, filtration have been used for a long time. Numerous new techniques have been developed in the 20 th century. One of these separation techniques uses membranes. Initially membranes were used during World War II in the Manhattan project for the separation of U^{235} and U^{238} from natural UF₆. These membranes were inorganic membranes. After this critical and very important starting point membrane research have been accelerated.

Membrane is a barrier which is capable of redistributing components in a fluid stream through a driving force such as difference in pressure, concentration or electrical potential. A schematic diagram of a membrane is given in Figure 1.2.

Membranes have some advantages over the conventional separation techniques. Membranes are very fast, efficient and economic in many cases. Membrane separation takes place without phase changes. Due to these reasons membrane processing is very popular nowadays. Many different types of membranes are in use these days with different sizes, structures and shapes and many others are in the research and development stage.



Figure 1.2. Schematic diagram for the membrane separation of gases.

The classification of membranes can be made in two main groups and many subgroups. Main groups are inorganic and polymeric (organic). And such a classification of membranes according to materials is given in Figure 1.3.



Figure 1.3. Classification of membranes based on their materials and structure.

Many different techniques such as sol-gel techniques, chemical vapor deposition, pyrolysis can be used for the production of porous ceramic asymmetric composite membranes. Sol-gel processing is a very new technique for membranes but this process have been widely used for the preparation of ceramic powders, fibers, coatings and monoliths.

The potential of membranes made of inorganic materials such as metals, ceramics, chemicals, and inorganic polymers were not widely recognized until high quality porous ceramic membranes were produced for industrial use on a large scale. Ceramic membranes are rapidly making inroads in wastewater and oil treatments, food and bevarage processing and biotechnology separations.

Dense (nonporous) membranes made of palladium and its alloys silver, nickel, and stabilized zirconia have been used or evaluated mostly for separating gaseous components. These membranes are limited in industrial practice and are permeable to ionic forms of hydrogen or oxygen.

Porous metallic membranes have been available for some time but due to their cost are not widely used. Porous ceramic membranes, such as alumina, glass and zirconia membranes with a pore diameter ranging from approximately 30 °A to 5 μ m are commercially available. Methods of membrane preparation microstructure, module configurations and applications are described in detail in the literature.

Porous inorganic membranes are generally superior to organic membranes in thermal, mechanical, and, structural stability without the problems of compaction or swelling, resistance to chemicals and microbiological attack, ease of cleaning and regenerating, and the ability to be backflushed, steam strerilized or autoclaved. These membranes have been used in liquid phase separations and in gaseous diffusuion for uranium recovery. Their potential application in areas such as gas separations and membrane reactors are in the research and development stage.

In the last decade, the so called "sol-gel" methods have been receiving a great deal of scientific attention among ceramic and glass scientists. These sol-gel methods offer new approaches to the preparation of glasses and ceramics. Despite the recent surge of scientific interest, the use of sol-gel methods in preparing glasses and ceramics are not new. The word "sol" describes the dispersion of colloids in liquids. Colloids are

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in turn described as solid particles with diameters in the range of $10 - 10000 \text{ A}^{\circ}$ each containing $10^3 - 10^9$ atoms. When the viscosity of a sol increases sufficiently, usually through the partial loss of its liquid phase, it becomes a rigid material which is termed as a "gel".

Sol-gel processes have been, however, more frequently utilized to prepare inorganic microporous membranes based on alumina, silica, titania and zirconia. Sol-gel chemistry appears to be well adapted for the synthesis of inorganic materials with pore diameters in the nanometer sizes.

In this research the preparation of ceramic membranes for gas separation applications by using sol-gel techniques were investigated. The effects of water/alkoxide ratio, H⁺/alkoxide ratio on the catalysis of the hydrolysis-condensation reactions and the peptization process were investigated by using N₂ adsorption-desorption isotherms, thermogravimetric analysis and FTIR (Fourier Transform Infra Red). The performance and the potential use of these materials in gas separation applications depend mainly on the ability in controlling-designing the microstructure-pore network in these materials.Polymeric silica particles were deposited on top of a support system consisting of a porous thick mesoporous γ -Al₂O₃ over a macroporous α -Al₂O₃ of desired thickness. These asymmetric membranes may be useful for the separation of gasses.

CHAPTER 2

MEMBRANE TYPES AND STRUCTURES

2.1 Polymeric Membranes

Polymers are defined as large molecules built up by the repetition of small, simple chemical units. The repetition may be linear or branched to form threedimensional networks. Polymers can exhibit two different states; rubbery and glassy states, depending on the temperature.

Polymers such as natural rubber, silicon rubber and siloxanes are in rubbery state at room temperature, i.e., their glass transition temperature T_g is too low. They show rubber like properties and membranes made up of rubbery polymers show high selectivities and low permeabilities. At sufficiently low temperatures, all amorphous polymers show the characteristics of glasses including hardness, stiffness and brittleness. Glassy polymers have low volume coefficient of expansion, a property which is associated with the glassy state. This low volume coefficient occurs as a result of a change in the slope of the curve of volume versus temperature at the point called glass-transition temperature (T_g). Polymers such as polysulfones, polyamides, polyacetates are in glassy state at room temperature so the membranes made up of these materials have glass like properties and have high permeabilities but low selectivities (1,13,14,51,72,73).

2.2 Inorganic Membranes

2.2.1 Types of Inorganic Membranes 2.2.1.1 Dynamic Membranes

Formation of the dynamic membranes are accomplished through film deposition on microporous supports or carriers from a feed solution of colloidal particles or solute component. Initiative research on dynamic membranes at Oak Ridge

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National Laboratory have been focussed on the retention of electrolytes. These membranes are known to deal with uncharged molecules. Their initial membranes were tailor made material and are available for specific applications in hyperfiltration and ultrafiltration.

A large variety of inorganic materials have been used like oxides of aluminum, iron, silicon, zirconium, rhodium, uranium and bentonite clay minerals for dynamic membrane preparation. Zirconia is a well known material used in dynamic membranes (1,4).

2.2.1.2 Dense Inorganic Membranes

The second type of inorganic membranes are called as dense membranes. They are thin sheets of metals or oxides. A good example is dense palladium and its alloys with Ruthenium, Nickel or other metals from group VI and VIII in the periodic table. These membranes are known as permeable to certain gases. These gases are hydrogen or oxygen and the gas transport mechanism is solution diffusion.

Catalytic reactions of hydrogenation or dehydrogenation are being carried out by using Pd-based membranes. These membranes cause increase in the selectivity and the yield. By using these membranes the yield increases from 14 % to 21 % in removing hydrogen from the dehydrogenation product of isopentene.

For oxidation of ethylene, amoniaethanol and ethylene nonporous silver has been used which is permeable selectively to oxygen. CaO stabilized zirconia membranes have been used for the thermal decomposition of CO_2 and water because of the permeation behaviour of oxygen.

A second form of dense membranes are called liquid immobilised membranes (LIM). Pores of these membranes are filled with a liquid and they are selective for certain compounds(1,4).

2.2.1.3 Porous Membranes

2.2.1.3.1 Metallic Membranes

Microporous metalic membranes can be prepared from metal alloys such as Ni, Al, Au, Cr, Pt, Pd by subsequent leaching of one component. These membranes have found their main application in gas separation processes. Porous metals are commercially available for particulate filtration. They are used in some cases as microfiltration membranes that can withstand harsh environments or may be supports for dynamic membranes.

Another important application of metallic membranes is in supplying highly pure hydrogen for semiconductor production. Nonporous metallic membranes are used for this purpose, operating at elevated temperatures. Pd and especially Pd- Ag alloys are particularly suitable membrane materials. These days Pd- Ag membranes dominate the market for two reasons; pure palladium is much more sensitive to fluctuations in thermal

stress because of charges in the microstructure after about 150 cycles from 25 to 700 $^{\circ}$ C and the permeability of pure palladium is low compared with that of an alloy containing about 23% of Ag.

Pd- Ag alloys are highly sensitive to traces of chlorine, arsenic, mercury and sulphur compounds, which react immediately with the membrane surface, causing permanent damage. Poisoning of the membrane caused by unsaturated hydrocarbons or the oxygen in inorganic compounds can be removed by flushing with nitrogen and filtered air at 400 $^{\circ}$ C (1,4).

2.1.3.2 Alumina Membranes

The market activities of alumina membranes thus far have provided the bulk of the momentum for making inorganic membranes an acceptable and viable separations tool in many applications. Currently, those alumina membranes having a pore diameter greater than approximately 0.1 μ m are made of α -alumina which is known to exhibit good stability thermally chemically and mechanically. Although it is stable up to about 1000 ° C, the α -alumina membrane modules are generally recommended below 140-150 °C for those applications where steam sterilisation is required (1,4,6,7,9,10).

This temperature limitation is a result of the common sealing and packing materials used presently. The α -alumina can be backflushed to provide periodic regeneration of the membranes, can also be steam sterilised and also chemically cleaned with caustic soda followed by nitric acid in the temperature range of 50-80 °C. They are generally not subject to any appreciable chemical attack particularly when exposed only periodically to strong acids and bases (1).

In contrast, transition- alumina membranes which are characteristically small in pore size are much less resistant to, for example, strong acids and bases, and can be dissolved in those chemicals with time. Therefore, they are not recommended for applications where strong acids or bases are either present in the feed streams or required as part of the cleaning procedure (1,4).

Alumina membranes have been used in a variety of applications like concentration of whole skimmed milk, clarification and sterilisation of fruit juices, wine, beer and malt, microfiltration of water, sterilisation in biotechnology and oilwater separation. The generally recommended operating cross-flow velocity is 1-7 m/s. Water permeability for 0.2 μ m and 4 nm membranes have been reported as approximately 3000 and 10 L/hm²bar respectively (1).

The porous alumina membranes have been used for gas separation in the isotopic separation and enrichment of uranium.

Porous nickel membranes with alumina coating separate H_2 from H_2S . Alumina membranes can effectively separate water vapour from air or alcohols. Two types of alumina membranes can be prepared 1) unsupported 2) supported ones. Membranes can be synthesised by using slip casting and sol-gel method(7,9,10).

Unsupported and supported α -alumina membranes can be prepared from boehmite colloidal suspensions. Boehmite sols were prepared by adding aluminum

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trisecbutoxide to distilled water then diluted nitric acid was added for peptization. The pore size of the alumina membranes can be tailor made by varying acid/hydroxide ratio, water/alkoxide ratio, acid type used in the preparation of the sol. (30,32,42,43,76,77).

Dipping time, the viscosity of the sol and the sintering temperature were effective in the formation of the membrane from the alumina sol. Many experimental studies showed that dipping time, number of dipping, alumina sol concentration at dipping control the membrane morphology, membrane thickness and permeability (8, 20, 36, 49, 52, 61).

Heat treatment schedules also affect pore size distributions and the pore structures of alumina gels. Another factor is the use of drying chemical control additives such as PVA, which can be added to boehmite sols and modify the drying and calcining procedures (16,17,18,19,54,74,80,81).

2.2.1.3.3 Zirconia Membranes

Various zirconia membrane systems come in the multiple tubular configuration, which may contain more than thousand tubes in a housing and use different porous supports. Like α -alumina membranes, zirconia membranes are stable over rather wide pH and relatively high temperature range, but their common uses are also limited to approximately 150 °C due to the potting compounds used for the construction of the modules.

Zirconia membranes have been applied in a number of industrial applications such as recovery of polyvinyl alcohol as the sizing chemical for the textile industry, separation of fresh cream cheese and extraction of serum proteins from whey, concentration of dilute latex wastewater, concentration of caustic extraction from Kraft bleach plant effluent and processing of soy and protein extracts (1,4).

Zirconia membranes on carbon support were originally developed by Union Carbide. Ucarsep and Carbosep are trade names of these ultrafiltration membranes. These membranes have high chemical resistance that allows steam sterilisation and cleaning procedures in the pH range of 0-14 at temperatures up to 80 $^{\circ}$ C (1,4).

Ultrafiltration top layer coating is applied to the macroporous carbon support. The coating material ; zirconia , have a particle size range 20 - 150 nm and aggregate size range of 100 - 1000 nm. Pore size of the carbon support is about 300 nm and 30 % porous. After coating membrane was applied it was heat treated at about 400 - 600 °C. Application areas of these membranes are treatment of water streams from oily wastes and food and dairy industry.

Guizard (10), Cot (5) and Larbot (37) used a sol-gel method to prepare zirconia membrane top layers on an alumina support. Zr alkoxide was hydrolysed at room temperature. The precipitate was peptised with nitric or hydrochloric acid at pH 1.1. Metal oxide percent of the final sol was about 20 wt %. Cot et al. (5) reported particle sizes of 10 nm for a low electrolyte concentration and if electrolyte concentration is 100 times higher, particle size increase to 60 nm. Particle size increases further if the ZrO_2 concentration in the solution is increased above 1 % (5,10,26,37).

Alumina supports were prepared by using slip casting process dried at 20-150 °C and thermal treatment applied in the 400- 900 °C The zirconia membrane layer can be produced by dipping processes, after dipping tetragonal phase exists at 700 °C. Pore diameter depends on the thermal treatment temperature and the pore diameter was 6 nm at 700°C and at 70 nm 1200 °C. Mean pore radiuos of this zirconia membrane was 32 nm (30).

These zirconia membranes can be used in ultrafiltration application such as separation of small biomolecules produced in bioreactors and for the partitioning of reactants and by-products.

2.2.1.3.4 Titania Membranes

In many studies titania membranes show excellent chemical resistance and interesting photochemical and catalytic properties (5,15,26,30,34,46,50,7,16,26). The simple fact that these materials have very high surface area makes them highly unstable at high temperatures because of their increased tendency to sinter (46,31).

Particle diameters were in the 6 to 180 nm range depending on the preparation condition. Titania is present in the anatase phase up to 500 °C and above this temperature is transformed to the rutile phase. Pore diameter depends on the calcination temperature, for example if it was calcined at 500 °C pore diameter was 6 nm and at 1100 °C pore diameter was 180 nm. It was necessary to use binders for the preparation of crack-free membranes (5,7,15,16,26).

Titania thin membrane layer can be produced from titania sol in isopropopanol at room temperature in an excess of a water/ isopropanol mixture to which a small amount of acid is added. Acid addition necessarry for the peptiaztion of the precipitate after hydrolysis. These peptised sols consisted of stable colloidal dispersions. Titania membranes were deposited on alumina supports from colloidal suspensions containing $0.1 - 0.2 \text{ mol/L TiO}_2$ after addition of drying control chemical additives (DCCA) such as polyvinyl alcohol (PVA) and / or hydroxy propyl cellulose(HPC) for preventing crack formation during the drying process. Thin titania layer was about 1 µm thick. These alumina supported titania mebranes used for measuring gas permeation. Mean pore diameters of the membranes after further heat treatment at T< 500 °C was 4-5 nm The pore diameter increased to around 20 nm due to the formation of the rutile phase at 600 °C (15,16,26,56,57,37). Titania membranes were chemically stable in wide pH ranges (2-12) in 10 weeks had a high water permeability (16).

Various gas separation experiment have been applied by using titania supported and unsupported membranes at different temperatures. For example He/O₂ gas mixture gave permselectivity of 2.49 at 25 °C and 2.74 at 245 °C (31,26,37).

2.2.1.3.5 Glass (Silica) Membranes

The preparation of submicrometer monodisperse particles by controlled hydrolysis of metal alkoxides has been widely investigated for a number of ceramic materials. In particular, sol-gel processes involving the formation of particulate materials or glass-precursor gels from silicon alkoxides such as tetraetylorthosilicate (TEOS) and tetrametoxysilane (TMOS). Silica sols and gels can be produced very easily both by the colloidal suspension and by the polymeric gel route. Larbot and coworkers (5) have described the synthesis of silica membranes starting with a commercially available silica sol in an aqueous solution at pH 8. In the preparation of silica sol starting from TEOS in ethonolic solution, the hydrolysis was performed under acidic conditions. Organic additives were used as binders along with glycol used as plasticisers to deposite at SiO₂ films on alumina porous substrates. The deposited films were dried and calcined at 450 °C (5,9,21,29,49,56,57,61).

Organic binder was added to the sol before coating in order to prevent crack formation during drying and firing treatments(55). Membrane pore diameter after calcination at 450 °C were in the 2nm - 6nm range. Peterson synthesised silica membranes with a mean pore diameter of 15°A. These membranes had a higher permeability to helium, nitrogen and oxygen then titania membranes. The result showed the permeability of these membranes to small molecules had a greater dependence on pressure(50).

Glass or silica membranes have been evaluated for desalination of sea and brackish waters and the removal of water from urea solutions by the principle of hydrofiltration, for reconcentration of oil in oil/water emulsions by high pressure ultrafiltration , for separation of metabolic products from blood, separation of protein and blood treatment by diafiltration (1,4).

2.2.1.3.6 Molecular Sieve Membranes

The main molecular sieve membranes are carbon and zeolite membranes. Zeolites are of great interest as new materials for inorganic membranes because the micropore systems of zeolites are inherent for the structure and their pore dimensions are precisely controllable by ion- exchange and chemical vapour deposition (55,56)

Synthetic zeolites are widely used in the form of granules, either as adsorptive separation agents or as catalysts. Zeolites with less than 10 °A pores are also desirable membrane materials, due to their crystallinity, resistance to high temperature and chemical inertness. Zeolites have been used as components in composite membranes. The most common form of these materials consists of a suspension of granular zeolitic particles in polymer and ceramic matrixes. Mechanical compression of a layer of powdered zeolite on a moulded alumina support, followed by NaOH and water glass treatment, produces a membrane that shows good air-separation properties (1,4).

Zeolite-filled hydrophobic membrane was introduced by Hennepe et al. The addition of silicate to silicone rubber membrane improved both the selectivity and flux of the membrane in alcohol separation from dilute mixtures. In some experimental work, various types of zeolite-filled hydrophilic membranes with polymer matrix were prepared for some separation experiment such as alcohol-water, acetone-water systems and various gas mixtures (O_2 , N_2 , CO, CO₂, H_2 , CH₄) (55, 56, 58, 59,33).

By using zeolite and silica, some researchers produced microcomposite system. Small crystals of zeolite with two and three dimensional channel systems were embedded in amorphous thin films derived from TEOS hydrolysed in alcoholic solution. These inorganic membranes will ultimately be deposited on the surface of chemical sensors and serve as moleculer sieves which control access of selected target molecules to the surface (13).

Molecular sieve carbon's (MSC) can be accomplished by the pyrolysis of thermosetting polymers such as polyvinylidene chloride, polyfurfuryl alchol, cellulose, cellulose triocetone (1980, 1986, 1987) By using polymers and MSC they produced hollow - fiber gas separation membranes. In principle, polymeric hollow fiber can be porous or dense. And they used this membranes for adsorption experiments of CO, CO_2 , O_2 , Ar, N_2 , C_2H_2 , H_2 , H_2O gases.Trimm and Coper (1970, 1973) prepared MSC for catalyst systems. (1)

2.2.2 Advantages and Disadvantages of Inorganic Membranes

2.2.2.1 Advantages

Major advantage of inorganic membranes is their high temperature stability. These membranes can be used for long term operations at high temperatures because of the thermal inertness. This is of special interest in applications in which the natural feed temperature is high or when it is desired to operate at high temperatures to decrease the viscosity of the feed by this way increasing membrane flux. Because of high thermal stability, these membranes can easily be used in steam cleaning and sanitising in food, dairy, beverage and pharmaceutical industry. In principle, determined by the membrane chemistry and stability of the components of the module, many inorganic membrane devices could operate at a temperature in excess of 1000 °C.

The second advantage is mechanical stability under large pressure gradients. Inorganic membranes are noncompressible and no creep formation occurs.

The other advantage of inorganic membranes are the chemical stability over a wide pH range. This advantage can be important for applications in which feeds with

extreme pH, especially on the alkaline side, are processed. It can also be used in cleaning cycles in which hot caustic or acid is used for cleaning.

These membranes have shown very long lifetime in many applications from 3 to 5 years. This reduce the operating costs for users.

Electrocatalytic and electrochemical activity easily realisable.

These membranes are easy to shape. Pore dimension and pore size distribution are also controlable.

An outstanding advantage of ceramic membranes is their ability to withstand prolonged exposure to non-aqueous media. This capability makes them suitable for hydrocarbon and various solvent applications, including operation at elavated temperature.

2.2.2.2 Disadvantages

Inorganic membranes have shown brittle character so need special configurations and supporting systems. This has been especially severe for modules constructed with individual tubular elements or with small diameter multiple-pass a way monoliths. This fragility problem should become relatively unimportant for larger diameter, less fragile monolith devices.

They have relatively high capital installation costs and also they have relatively high modification costs in case of defects. Compact, polymeric membrane modules have had prices from \$8 to \$20 per square foot. Ceramic membranes have had prices of \$150 to \$200 per square foot. Nowadays some modules are becoming available at a price as low as \$120 per square foot. These high prices for ceramic membrane products do not reflect a high profit for the manufactures, but a high production coast. As illustrated in the market place, ceramic membranes can displace polymeric membranes only if a) Ceramic membranes can perform a separation which cannot be actieved with polymeric products, such as producing very high solid concentrates or operating at high temperature b) operating conditions allow a considerable high membrane flux for the ceramic membrane products Ceramic ultrafiltration membranes have been reliably produced with retention properties comparable to those of the lowest "molecular weight cutoff" polymeric membranes. This is important in applications in which loss of product for example protein in whey recovery, carries on economic penalty

Ceramic ultrafiltration membranes have low water flux which will limit process flux in many applications.

These membranes show brittle character needs special configuration and supporting systems.

CHAPTER 3

USE OF INORGANIC MEMBRANES IN ULTRAFILTRATION, MICROFILTRATION AND GAS SEPARATION

The technologies in which ceramic membranes are used include Microfiltration, Ultrafiltration, Gas separation and pervaporation. Microfiltration membranes have relatively large pores (100nm to few μ m in size), Ultrafiltration membranes especially with pore size in the 1 nm- 100nm range. Nanofiltration membranes for gas separation and pervaporation with pore size of 1nm or smaller. Mesopores generally are defined as those having widths between 20 and 500 A (2 and 50 nm), macropores those with widths greater than 500 A and micropores those with widths smaller than 20 A (1,2,3,4,5,6,71).

Historically membrane experiments started at 1823 from Dutrochet for osmosis and dialysis work. But the first large scale application of inorganic membranes was for the separation of U^{235} and U^{238} from natural UF₆ mixture during World War II in the Manhattan Project . In 1970's inorganic membranes started to be used for gas separation, before the 1970's membranes relatively used in food and bevarage processes, biotechnology application and water treatment. The present and possible known application of ceramic membranes are given Table 3.1 and the share of markets for advanced separation systems in 1991 in Figure 3.1. Table 3.1. Applications for Ceramic membranes (3).

Indusry	Use	
Food and Beverages	Clarifies and strerilizes fruit juices and vinegar; concentrates and homogenizes milk and eggs; separates constituents in whey removes phenols, tannins, colors and heat-unstable proteins for wine	
Gas Separation	Removes hydrogen from refinerystream and CO ₂ and H ₂ S from natural gas; N ₂ enrichment; CH ₄ recovery in mining operations	
Biotechnology/Pharmaceutical	Concentrates vaccines and enzymespurifies amino acids, vitamins and organic acids removes viruses from culture broths	
Petrochemical	Waste-oil hydrogenation processes, catalytical dehdrogenation of large molecules at low temperatures and pressures, coal gasification	
Metal Refining	Removes impurities and undesirable metal oxides for molten aluminum, magnesium, and superalloys	
Electronic	Purification for water, acids, solvents and organic compounds	

PROCESS





Ultrafiltration in the conventional sense is a pressure-driven process often used for simultaneously purifying, concentrating and fractionating macro molecules or fine colloidal suspensions without phase change or interphase mass transfer. Ultrafiltration membranes typically have pore sizes in the range from 10 to 1000 °A . Typically rejected species include sugars, biomolecules, polymers and colloidal particles.

Ultrafiltration membrane processes are generally used in the food, bevrage and dairy industries for effluent treated and for biotechnology and medical applications. In Table 3.3 has been shown some of the current and future uses of ultrafiltration membranes in various industries.

Microfiltration is the process to separate micron-sized particles from fluids. Approximate range of the microfiltration membrane is 0.02 to 10 μ m. Microfiltration membrane modules are typically operated in one of two modes, cross flow or through flow. Cross flow microfiltration is becomming increasingly popular as the preffered mode for a large variety of filtration applications involving separation and concentration of particulate suspension or solutions, the recovery of low molecular weight substances and in some instances the recovery of low molecular wieght substances and in some instances the recovery of molecular such as proteins.

Recently much attention has been paid to ceramic membranes exhibiting a nanoporous structure with the aim of new membrane processes for the nanofiltration of liquids, pervaporation gas separation or catalysis. These membranes are achievable using the concept of nanopahse ceramics. Nanophase materials deal both with the nanometer- sized particle and with the nanometer pore size aspects. The nanopore aspects is central to membrane technologies because of the need for selective separation process at the molecular level.Membrane separation processes are tabulated at Table 3.2.

Table 3.2. Membrane separation processes.

Membrane Process	Separation Potential for	Driving force	Preferably permeating component
Reverse Osmosis	Aqueous low molecular mass solutions Aqueous organic solutions	Pressure difference	Solvent
Ultrafiltration	Macromolecular solutions, emulsions	Pressure difference	Solvent
Microfiltration	Suspension, emulsions	Pressure difference	Continuous phase
Gas permeation	Gas mixtures, water vapour-gas mixtures	Pressure difference	Preferably permeating component
Pervaporation	Organic mixtures, aqueous-organic mixtures	s Permeate side: ratio of partial pressure to saturation pressure	Preferably permeating component
Liquid membrane	Aqueous low molecular mass solutions, aqueous-organic solutions	Concentration difference	Solute (ions)
Osmosis	Aqueous solutions	Concentration difference	Solvent
Dialysis	Aqueous solutions	Concentration difference	Solute (ions)
Electrodialysis	Aqueous solutions	Electric field	Solute (ions)

Table 3.3. Ultrafiltration Applications (3).

Industry	Existing	Emerging
Metal Finishing	Electropaint, oil/water emulsions	Spray paint
Metal Working	Oil/water emulsions	Lubricating oils
Dairy	Whey proteins, milk	Protein hydrolysis
Pharmaceuticals	Enzymes, vaccines, plasma proteins, antibiotics, progens	Bioreactor
Food	Potato starch, egg white,gela and wine Clarification	Vegatable oils
Textile	Sizing chemicals, indigo scouring	
Pulp Paper	Lignin compounds	
Chemicals	Waste latex, in-process latex	
Leather Working		Tannery waste
Sewage	Sewage treatments for buildings	Municipal waste
Water	Water purufication, reverse osmosis pretreatment	
CHAPTER 4

SOL-GEL PROCESSING OF CERAMIC MEMBRANES

Sol-gel processes provide a new approach to the preparation of metal oxides. Starting from a solution, a solid network is progressively formed via inorganic polymerization reactions. The term sol-gel processing could actually be used in a broader sense to describe the synthesis of inorganic oxides by wet chemistry methods such as precipitation, co-precipitation or hydrothermal synthesis.

As early as 1845, Selmi had produced silver chloride sols and noted that salt solutions greatly affected the stability of the colloid, i.e they caused the particles to settle out. Faraday observed that dispersions could scatter light proving that the salts were not in solution, but present as discreet particles. It is, however only comparatively recently that industry has been able to capitalise on the benefits of these sol-gel reactions, as both technical and economic factors inhibited their full-scale exploitation (41,65).

Inorganic sol-gel routes were pioneered in the 1960s by OAK Ridge Laboratories (USA) and the Erwell Laboratories (UK). Their work was focused on applications in the nuclear industry, where remote handling of powders and the elimination of dusty processes were of paramount importance and for these reasons cost penalties could be tolerated more easily. The initial studies were focused on uranium and thorium oxides but were later extended to ceramics. It proved possible, using sol-gel techniques, to produce ceramic powders having specific particle size and densities. This eliminates the crushing and grinding steps required by conventional processes. The advantage of these techniques offered in the control of particle morphology was soon extended to non-nuclear applications, and there has been a huge interest in these techniques.

This expansion of interest in these techniques in the 1960s also broadened the applications for metal alkoxides in ceramics and glasses. A strong interest in these materials continues particularly in electronic and structural applications. These application

areas include high-tech ceramics such as piezoelectric, pyroelectric and superconducting materials. There have also been significant advances made in contact lenses, filters, catalyst supports and membranes. Some patented applications include ceramic fibers and abrasives.

Although considerable investment was made in coatings research very little of the work was translated into products. However, the pioneering work of Yoldas and Dislich and Hussman (in coatings) has led to a major revival of interest in these areas. One of the successes of this revival is the development of thin film ferroelectric non-volatile memories (62).

Two routes are currently used depending on the nature of the molecular precursor. The inorganic routes are currently used depending on the nature with metal salts in aqueous solutions and the metal organic route with metal alkoxide or by changing the pH of an aqueous solution. Condensation that occurs leading to the formation of metal-oxygen metal bonds. Condensed species are progressively formed from the solution leading to oligomers, oxopolymers, colloids, gels or precipitates. Oxopolymers and colloidal particles give rise to sols, which can be shaped, gelled, dried and densified in order to get powders, films, fibers or monolithic glasses (63).

Sol-gel processes offer many advantages as compare to the conventional powder route such as:

1- Homogenous multi-component systems can be easily obtained by mixing the molecular precursor solutions.

2- The potential ability in a viscous liquid to minimise the sources of defects introduced in the processing powder.

3- The ability to visually examine many gel products for defects after drying.

4- Temperatures required for material processing can be easily obtained by mixing the molecular glasses or ceramics.

5- The rheological properties of sols or gels allow the formation of fibers, films or composites by such techniques as spinning, dip-coating or impregnation. (64)

One unique property of the sol-gel process is the ability to go all the way from the molecular precursor to the product, allowing a better control of the whole processes and synthesis of tailor-made materials. Therefore, a real mastery of the sol-gel process would require an emphasis which relates chemical reactivity to gel formation and powder morphology.(65)

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The chemistry of the sol-gel process is based on hydroxylation and condensation of molecular precursors. These reactions have been extensively studied in case of silica. Two different routes are usually described in the literature depending on whether the precursor is an aqueous solution of an inorganic salt or a metal organic compound.

The most versatile precursors for the sol-gel synthesis of oxides are undoubtedly metal alkoxide, which are very reactive toward nucleophilic reagents such as water. Hydrolysis and condensation of transition metal alkoxide appear to be much more complex than silicon alkoxide. They must be handled with great care, in a dry environment and stabilised via chemical modification.

Structural evaluation during the sol to gel and gel to solid transitions need to be fully understood before a real mastery of the sol-gel process can be reached. The properties of a gel and its response to heat treatment are very sensitive to the structure already created during the sol stage. Therefore the formation of colloidal aggregates often determines the main properties of the resulting powder and its ability for the extent to which the powder can be sintered. By varying the chemical conditions under which silica is polymerised, polymers to colloidal particles. The aggregation of colloidal SiO₂ particles and the growth of silica polymers have been extensively studied during last few years.

Monodispersed transition metal oxide colloids are currently synthesised which can exhibit anisotropic shapes. Particle-particle interactions then lead to the formation of anisotropic aggregates in which all individual particles are mutually oriented. These ordered aggregates called "tactoids". They can lead to anisotropic coatings that behave as host structures for intercalation.

Sols and gels are usually considered as intermediates in the processing of glasses and ceramics. Therefore drying and densification are very important processes that need to be fully understood (63).

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4.1 Sol - Gel Chemistry

4.1.1 Hydrolysis of metal cations

The word "hydrolysis" is used here to describe those reactions of metal cations with water that liberate protons and produce hydroxy or oxy species. In aqueous solutions this reaction results from the solvation of positively charged cations by dipolar water molecules. It leads to the formation of $[M(OH_2)_N]^{z+}$ species.

 $H \qquad H$ $M^{2^{+}} + : O \rightarrow [M \leftarrow O]$ $H \qquad H$

Water is a Lewis base and the formation of an M= OH bond with the metal cation (Lewis acid) draws electrons away from the bonding σ molecular orbital of water molecule. This electron transfer weakens the O-H bond and coordinated water molecules behave as stronger acids than the solvent water molecules. Spontaneously deportation then takes place follows:

$$[M(OH_2)_N]^{z_+} + hH_2O == [M(OH)_h(OH_2)_{N-h}]^{(z-h)_+} + hH_3O^+$$
(1)

Where "h" is called the hydrolysis ratio. It indicates how many protons have been removed from the solvation sphere of the metal cation. The acidity of coordinated water molecules increases as the electron transfer within the M-O bond increases. In dilute solutions this leads to a whole set of more or less deprotonated species ranging from aquaocations $[M(OH_2)_N]^{z+}$ (h=0) to neutral hydroxides $[M(OH)z]^0$ (h=z) or even oxyanions $[MO_{N'}]^{(2N'-z)-}$ corresponding to the case when all protons have been removed from the coordination sphere of the metal. The electron transfer within the M \leftarrow OH₂ bond increases with the oxidation state of the metal cation N^{z+} and coordinated water molecules become more acidic as z increases as shown in Table 4.1.

M ^{z+}	X	δ _M	δο	δ _H
Mg ²⁺	2.625	+0.86	-0.34	+0.27
Al ³⁺	2.754	+0.78	-0.29	+0.33
Ti ⁴⁺	2.875	+0.76	-0.25	+0.39
V ⁵⁺	3.023	0.51	-0.19	+0.47
W ⁶⁺	3.283	+0.31	-0.09	+0.60

Table 4.1 . Partial charge distribution in $[M(OH_2)_6]^{z+}$ (41).

A convenient rule- of-thumb shows that the hydrolysis ratio h of a given precursor $[M(OH)_h(OH_2)_{N-h}]^{(z-h)+}$ mainly depends on two parameters, the pH of the solution and the oxidation state of the metal cation M^{z+}. A charge- pH diagram can then be drawn in order to show which aqueous species predominate in Fig.4.1. Two lines corresponding to h=1 and h=2N-1 respectively separate three domains in which H₂O, OH, O⁻² ligands are observed. (67)



Figure 4.1. Charge- pH diagram showing the evoluation of hydrolysed species (65).

4.1.2 Determination of the hydrolysis ratio

In very dilute aqueous solutions, metal cations exhibit several hydrolysed monomeric species in the pH range 0- 14. The problem is then to know whether it is possible to predict the chemical nature of these aqueous species at a given pH.

Following the electronegativity equalisation principle it can be stated that deportation (eq. 1) goes on until the electronegativity X_h of hydrolysed species $[M(OH)_h(OH)_{N-h}]^{(z-h)+}$ becomes equal to the mean electronegativity. Xaq of the aqueous solution.

Proton exchange reactions between H_3O^+ and H_2O species are very rapid aqueous solution so that it can be assumed that $X_H^+ = Xaq$. As a consequence a linear relationship can also be established between the mean electronegativity Xaq and the pH of an aqueous solution.

$$Xaq = Xaq^{\circ} - \lambda pH$$
 (2)

Xaq° and λ depend on the reference state for electronegativity scale. Choosing $[H_5O_2]^+$ as a reference for proton at pH=0 and 2.49 as the mean electronegativity of water at pH=7 to:

$$Xaq=2.732 - 0.035pH$$
 (3)

This means that h can be expressed as a function of pH leading to the following expression:

at pH= 0
$$h = 1.47z - 0.5N - 1.08(2.732 - X_M) / (X_M)^{1/2}$$
 (4)

at pH=14
$$h= 1.08z + 0.37N' - 0.79(2.242 - X_M) / (X_M)^{1/2}$$
 (5)

This show that at a given pH, h mainly depends on the oxidation state "z" and the coordination number "N" of the cation M^{z+} (41).

4.1.3 Hydrolysis of Si $^{\rm IV}$ and Al $^{\rm III}$

The Partial Charge Model, applied to Si^{IV} (X_{Si}= 1.74, N=4) leads to:

$$h = (2.088 + 0.217 \text{pH}) / (0.679 + 0.018 \text{pH})$$
(6)

Four different hydrolysed precursors $[H_n(SiO_4)^{(4-n)}$ can be found in aqueous solutions, ranging from $[Si(OH)_3(OH)_2]^+$ (h=3) to $(SiO_2(OH)_2)^2$ at pH=14 shown in Fig 4.2.



Figure 4.2 . Hydrolysis of Si $_{IV}$ (N=4) and Al^{III} (N=6, N'= 6) as function of pH (41).

Aluminium provides a more interesting example for which the coordination of the metal cation decreases from octahedral as pH increases. This coordination change occurs around pH=6.

Let us consider the M-OH₂ bond. The negatively charged oxygen atom gives electrons to both the metal M and the hydrogen: $M\delta^+ \iff O\delta^- \Rightarrow H^{\delta^+}$ deportation goes on, electrons are more attracted by the metal. The partial charge δ_M becomes less positive and the M-O bond becomes less polar Table 4.2 shows, leading to covalent anions such as $[AIO_4]^{5-}$ Octahedral aluminium $[Al(OH_2)_6]^{3+}$ species are observed at low pH whereas tetrahedral aluminates $[Al(OH)_4]$ - are formed at high pH as shown in Fig 4.2.

Table 4.2. Partial charge in hydrolysed A^{III} species (41).

Precursor	X	δ _{Al}	δ(H ₂ O)
$[Al(OH_2)_6]^{3+}$	2.75	+0.78	+0.37
$[Al(OH)(OH_2)_5]^{2+}$	2.67	+0.73	+0.26
$[Al(OH)_2(OH_2)_4]^+$	2.59	+0.68	+0.14
[Al(OH) ₃ (OH ₂) ₃]°	2.49	+0.62	0

4.1.4 Stability of M-OH bonds

According to Figure 4.1 the order of preference for ligands is usually $H_2O < OH^- < O^{2-}$ as the (charge/ radius) ratio of the cation increases (Fig.5.1). However M-OH bonds are always stable in aqueous solutions. The high dielectric constant of water can lead to the dissociation of polar bonds. The stability of $M^{\delta+} - O^{\delta-} - H^{\delta+}$ bonds toward ionic dissociation then depends on the electronegativity of the metal.

Basic dissociation is observed with low-valent metal cations such as Na⁺ or Ba²⁺. Their electronegativity is so small (X_M <1) that electrons are strongly attracted toward the OH group leading to the dissociation of the polar $M^{\delta-}$ - OH^{$\delta-$} bond: M-OH_{aq} \Rightarrow M⁺_{aq} + OH_{aq}. NaOH is a strong base and [Na (OH₂)_N] cannot be deprotonated under usual conditions.

Acid dissociation is observed with electronegative elements at the upper right of the periodic table (P^{V} , S^{VI} , CI^{VII}) or with highly charged " d⁰" metal cations such as Mn ^{VII} that give covalent oxyanions. These cations are more electronegative than hydrogen (X_{H} = 2.1). Electrons are attracted toward the metal, increasing the positive charge H^{δ+} leading to the dissociation of the highly polar MO^{δ-} - H^{δ+} bond: MO⁻ H_{aq} \Rightarrow MO⁻_{aq} + H⁺aq. HMnO₄ is a very strong acid and [MnO₄]⁻ species cannot be protonated even at low pH.

M-OH bonds are stable either when transition metal ions have a high oxidation state and empty "d" orbitales. Strong $d\pi$ - $p\pi$ transfers favour the formation of M= O double bonds which decrease the positive charge of the metal ion (65).

4.2 CONDENSATION OF HYDROLYZED PRECURSORS

The "charge-pH" diagram is a very useful guide for sol-gel chemistry. Condensation becomes possible when at least one stable M-OH bond is formed i.e. in the intermediate domain in Figure 4.2.

Condensation could also be initiated via redox reactions. MnO_2 gels for instance cannot be formed Mn^{IV} precursors that are usually not soluble in aqueous solutions. They have been prepared via the reduction of permanganate salts $[MnO_4]^2$ by fumaric acid.

The enthalpy changes for the first hydrolysis reaction is positive and often close to the enthalpy of dissociation for water (13.3 kcal/mole). The tendency of metal cations to hydrolyse therefore increases with temperature, a phenomenon which is widely used for the hydrothermal synthesis of molecular sieves or monodispersed colloids (64).

4.2.1 Olation and oxolation

The two main mechanisms for condensation are called olation and oxolation. In both cases, polynuclear species are formed via the elimination of water molecules from precursors containing at least one M-OH group.

Olation corresponds to the nucleophilic addition of a negatively charged OH group onto a positively charged hydrated metal cation. As aqua-cations usually exhibit their maximum coordination number, the formation of an "ol" bridge requires the departure of one molecule of water as follows:

$$M-OH^{\delta-} + M^{\delta+} - OH_2 \Longrightarrow M-OH-M^{\delta+} - OH_2^{\delta+} \Longrightarrow M-OH-M + H_2O$$
(7)

Oxolation involves the condensation of two OH groups to form one water molecule, which is then removed giving rise to an "oxo" bridge as follows:

$$> M - OH + HO - M < == > M - O - M < + H_2O$$
 (8)

Olation and oxolation require at least one negatively charged nucleophilic OH group in the coordination sphere of the metal cation. However a survey of experimental data suggests that this is not enough and condensation does not seem to occur at room temperature when the positive charge of the metal cations is too small ($\delta_M \leq +0.3$) (68).

4.2.2 Condensation of a tetravalent cation, Si ^{IV}

The aqueous chemistry of Si^{IV} is dominated by the fact that it remains tetrahedrally coordinated over the whole range of pH. Condensation occurs upon acidification of an aqueous solution silicate. Condensed phases are formed of corner sharing [SiO4)⁴⁻ tetrahedra in order to minimise electrostatic repulsion between cations.

As shown in the first part of Table 4.3, only protonated species $[H_nSiO_4]^{(4-n)}$ have to be taken into account as precursors for condensation.

Precursor	hydrolysis	PH	X ·	δ _{Si}	бон
[H ₅ SiO ₄] ⁺	h=3	< 0	2.74	+0.56	0
$[H_4SiO_4]^0$	h=4	9.99	2.58	+0.47	-0.12
[H ₃ SiO ₄] ⁻	h=5	13	2.3	+0.35	-0.30
$\left[\mathrm{H_{2}SiO_{4}}\right]^{2-}$	h=6		2.10	+0.2	-0.55

Table 4.3. Partial charge calculation on $[H_nSiO_4]^{(4-n)}$ (41).

The $[H_2SiO_4)^{2-}$ precursor (h=6) is a strong acid. They can only be observed in very basic or acid aqueous solutions respectively. The pH= 5 precursor $[H_3SiO_4]^-$ leads to the formation of a large number of oligometric species around pH=12. About 20 different species ranging from monomers to decamers have been evidenced by Si NMR in aqueous solution of potassium silicate. Reported data shows that above pH=9.

In the pH range $3 \le pH \le 9$, neutral species Si(OH)₄ are predominant they lead, via oxolation reactions, to the formation of amorphous hydrated silica: Si(OH)₄ == SiO₂ + 2H₂O. Around the Point of Zero Charge (pH=3), gelation is very slow but reaction rates increase significantly by changing the pH. Base catalysis occurs at higher pH. It is governed by nucleophilic addition of negatively charged Si-O onto positively charged Si atoms. This leads to branched species, which give rise to dense colloidal silica particles (Fig.4.3).

Acid catalysis (pH< 2) leads to the protonation of the leaving silanol group. The more negative OH groups are then involved, i.e. terminal si-OH rather than bridging Si-OH-Si. This leads to the formation of chain polymers, which give rise to polymeric gels. As shown in Fig.4.3 (41).



Figure 4.3. Polymerization behaviour of silica (25).

4.3 ALKOXIDE PRECURSORS

The sol-gel synthesis of glasses and ceramics is mainly based on the hydrolysis and condensation of alkoxide precursors. These alkoxides are not soluble in water and common solvent such as the parent alcohol has to be used. Water is typically diluted in an alcohol and added slowly to the alkoxide solution in order to prevent precipitation.

The metal- organic route is much more versatile than the inorganic one. Many chemical parameters, other than pH can be used to control the reactions (solvent, hydrolysis ratio, alkoxy group, acid or base catalysis). However alkoxides are rather expensive and highly reactive toward moisture. Therefore they are not currently used in industry and most research is performed in universities. The sol-gel chemistry of alkoxides is somewhat different from the chemistry of aqueous solutions. However, as soon as an excess of water is added, most organic groups are removed and chemical reactions became similar to those observed in aqueous solutions.

4.3.1 Hydrolysis and Condensation of Metal Alkoxides

The so-called sol-gel process is based on the hydrolysis and condensation of molecular precursors such as metal alkoxides M(OR)z where R is typically an alkyl group (R=CH₃, C₂H₅,)

$$Hydrolysis: > M - OR + H_2O == > M - OH + ROH$$
(9)

$$Condensation: > M - OH + RO - M < == > M - O - M < + ROH$$
(10)

Where M can be Si, Ti, Al, Zr. These reactions can happen under acidic, basic, or neutral conditions (34,26). The formation of gels for acid and base catalysed systems is shown schematically in Figure 4.4. Figure 4.4-a) acid - catalysed gels, b) base-catalysed gels, c) colloidal gel aged under conditions of high solubility, d) colloidal gel. Composed of weakly bonded particles (69).



Figure 4.4. Schematic representation of gel desiccation (69).

They can be synthesised directly via the reduction of alcohols by strongly electropositive metals or via substitution reactions of metal salts such as chlorides with alcohols or alkaline alkoxides.

Alkoxy groups are rather hard π - donor ligands. They stabilise the highest oxidation number of the metal. Therefore alkoxides of main group elements and d^o transition metals are well known while those corresponding to soft an late transition metals have been much less studied. The number and stability of metal alkoxides decrease from left to right across the periodic table.

The chemical reactivity of metal alkoxides toward hydrolysis and condensation mainly depends on the positive charge of the metal atom δ_M and its ability to increase its

coordination number "N". As a general rule, the electronegativity of metal atom decreases and their size increases when going toward the bottom left of the periodic table as shown in Table 4.4. The corresponding alkoxides become progressively more reactive toward hydrolysis and condensation. Silicon alkoxides are rather stable while cerium alkoxide are very sensitive to moisture. Alkoxides of electropositive metals must be handled with care under a dry atmosphere otherwise precipitation occurs as soon as water is present. Alkoxides of highly electronegative elements such as $PO(OEt)_3$ cannot be hydrolysed under ambient conditions, whereas the corresponding vanadium derivatives $VO(OEt)_3$ are readily hydrolysed into vanadium pentoxide gels (41,65,67)

Table 4.4. Electronegativity "X", partial charge " δ_M ", ionic radius "r" and maximum coordination number "N" of some metal alkoxides (41).

Alkoxide	X	δ _M	r (Å)	N
Si(Opri)4	1.74	+0.32	0.40	4
Ti(Opri)4	1.32	+0.60	0.64	6
Zr(Opri)4	1.29	+0.64	0.87	7
Ce(Opri)4	1.17	+0.75	1.02	8
PO(Oet)3	2.11	+0.13	0.34	4
VO(Oet)3	1.56	+0.46	0.59	6

4.3.2 Sol-Gel Chemistry of Silicon Alkoxides

The sol-gel chemistry of silicon alkoxides has been extensively described. It is very different from the chemistry of silicates in aqueous solutions.

Hydrolysis and condensation reactions of Silica could be written as follows:

$$Si(OR)_{4} + H_{2}O \rightarrow Si(OR)_{3}(OH) + ROH$$
(11)

$$Si(OR)_{3}(OH) + Si(OR)_{4} \rightarrow (RO)_{3}Si-O-Si(OR)_{3} + ROH$$
(12)

$$2Si(OR)_{3}OH \rightarrow (RO)_{3}Si-O-Si(OR)_{3} + H_{2}O$$
(13)

The hydrolysis of $Si(OR)_4$ then leads to $Si(OH)_4$ and the formation of SiO_2 .

Si ^{IV} is fourfold coordinated (N=Z=+) in the precursor as well as in the oxide so that coordination expansion does not occur and silicon alkoxides Si(OR)₄ are always monomeric. The electronegativity of Si is rather high (X=1.74) and its positive charge $(\delta \approx +0.3)$ quite small. Silicon alkoxides are therefore not very sensitive toward hydrolysis. Gelation can take several days. Their reactivity decreases when the size of alkoxy groups increases. This is mainly due to steric hindrance, which prevents the formation of hypervalent silicon intermediates.

As for aqueous solutions, hydrolysis and condensation rates of silicon alkoxides can be enhanced by acid or base catalysis. Inorganic acids reversibly protonate negatively charged alkoxide ligands and increase the reaction kinetics by producing better leaving groups. Basic catalysis provides better nucleophilic OH⁻ groups for hydrolysis whereas deprotonated silonol groups Si-O⁻ enhance condensation rates.

Acid catalysis mainly increases hydrolysis rates whereas basic catalysis enhances condensation.

However catalysis does not only increase reaction rates. As in aqueous solutions, it leads to polymeric species to polymeric species of different shapes. The negative charge of OR groups increases as the electron-providing power of oxo and alkoxo ligands increases. The ease of protonation of OR groups therefore decreases as the connectivity of the adjacent Si atom increases. Acid catalysed condensation is directed preferentially toward the ends of oligomeric species resulting in chain polymers. The positive partial charge δ_{Si} increases with its connectivity so that nucleophilic addition of Si-O⁻ is directed preferentially toward the middles of oligomers leading to more compact, highly branched species.

4.4 Preparation of Sols

There are two main routes for the sol-gel process, which are described in Fig. 4.5. The route on the left side is known as the colloidal (or particulate) route. It involves the reaction of a metal salt or hydrated oxide with excess water. This yields a precipitate of gelatinous hydroxide colloidal particles, which can redisperse through a peptization reaction using an electrolyte. The particle sizes in the resulting sol are typically a few tens of nanometres an are suitable to create microporous (1-20 Å) or mesoporus (20-60 Å).



Figure 4.5. The two routes used to produce inorganic membranes.

In the colloidal gel route due to faster hydrolysis rates, a gelatinous precipitate is obtained which is peptized usually with some amount of acid to form a stable colloidal sol.

Upon the extraction of the solvent from these polymeric and colloidal gels solids with different pore structures will form: This is again schematically shown in Figure 4.6 and 4.7 for the silica system.

Certain parameters such as water/alkoxide ratio, molecular separation by dilution, the reaction medium, the nature of catalyst, pH etc. will effect the average molecular size distribution of the polymeric species. This is in turn will make it possible to obtain materials with different properties.



Figure 4.6. Polymer growth and gel formation in acid catalysed systems (25) Figure 4.7. Polymer growth and gel formation in base-catalysed systems. The porous structure and pore size distributions are governed by particle aggregation at the sol stage. The peptization phenomenon used to prepare a colloidal sol is based on electrostatic interactions according to DLVO theory. The repulsion forces that prevent particle aggregation in the sol are a result of the electrical double layer caused by the amphoteric behaviour of the most of the oxide surfaces.

Electrophoresis allows us to determine the particle stability range through particle mobility measurement as a function of pH and electrolyte concentration. When the pH value is decreased or increased away from the isoelectric point (IEP), a maximum stability for the sol is observed with high repulsive forces between particles.

Near the IEP a flocculation phenomenon occurs, resulting in Fig.4.8, a charge in a particle mobility versus pH results in an evolution of particle stacking, which influences pore size and the structure of the membrane. Based on the control of these phenomena, tailored pore structures have been produced for titania and zirconia membranes. This concept was also applied to alumina membranes. The pore sizes were in the 2.5-6 nm range. Drying and firing steps can also be porous structure in different ways. The influence of drying conditions was revealed to be of prime importance to silica membranes. Concerning the firing step, Fig. 4.9 illustrates the influence of temperature on pore size evolution for an alumina membrane (66).



Figure 4.8. Influence of particle charge and mobility in a colloidal sol on the porosity of the resulting material. V=potential energy, H= interparticle distance. (66).



Figure 4.9. Influence of the firing temperature on the pore size evolution of an alumina membrane (66).

4.5 Aging and Desication

Although the sharp increase in viscosity, which accompanies gelation, essentially freezes in a particular polymer structure at the gel point (ie. gelation may be considered a rapid solidification process). This "frozen-in" structure may change appreciably with time (aging) depending on the temperature, solvent and pH conditions or upon removal of solvent (desiccation). Changes in gel structure during aging and desiccation were described by Zarzycki et al. with respect to the problem of preparing monolithic gels. They described the structures of gels (prepared either by destabilisation of silica sols or polycondensation of organometallic compounds) according to Iler's models of aqueous silicates and thus made no distinction between "polymeric" and colloidal gels. However, there is now compelling evidence that under many conditions employed in gel preparation, single phase polymer gels rather than colloidal gels are formed. This may change the mechanism of aging and desiccation significantly.

For example, because of the similarity in structure of certain metal alkoxide derived gels and organic polymer gels such as polyacrylamides (both systems are composed weakly branched polymers and are single phase at the gel point), Schafer and Keefer recently postulated that critical phenomena such as phase separation should be observed in these inorganic systems as well. According to theories established by Tanaka and others for organic polymer gels changes in temperature, solvent quality or solvent concentration can induce phase separation (which is observed to occur reversibly in poyacrylamide gels). It is expected, however, that as the critical point is approached, e.g. during a change in concentration, fluctuation in polymer density grow larger in amplitude (than those resulting merely from thermal motions) and scale as the gel separates into regions of high and low polymer density. Density fluctuation should promote additional crosslinking as unreacted terminal groups (OH and OR) come in contact in regions of higher polymer density. This increased crosslinking and because under most conditions the rate of depolymerisation is low should cause phase separation to be essentially irreversible (69,70).

Qualitative evidence in support of phase separation has been observed by Yoldas. In several reports, he shows a gel prepared from a titanium alkoxide which, under particular aging condition is shown to have shrunk dramatically while expelling solvent. This may represent a phase separated system gradually approaching equilibrium (34).

Much of the current interest in gels stems from the potential of forming monolithic pieces of glass. As a part of this process gels must be dried without cracking. Changes in gel structure during drying were described by Iler for colloidal systems. According to Iler, surface tension forces created during solvent removal cause the original extended network to fold or crumple as the coordination number of the particle increased. Porosity develops when due to additional crosslinking or neck formation, the gel network becomes sufficiently strengthened so that it resists the compressive forces of surface tension. Thus the final desiccated gel structure (xerogel) will be a contracted and distorted version of the structure of the gel originally formed in solution (Figure 4.4 c & d) (68).

For polymer gels, removal of solvent is expected to collapse the network gradually resulting in additional crosslinking as unreacted hydroxyl and alkoxy groups come in contact. If so, the resulting phase separated structure may bear no relation to the structure of the gel originally formed in solution, and hence the final desiccated morphology may present only a contracted version of this secondary phase separated structure.

If phase separation does not occur (e.g. if it is unfavourable thermodynamically or kinetically) it is expected that polymer gels will continue to collapse and crosslink until they can resist the compressive action of surface tension (at which point porosity is created).

High density, low pore volume gels are therefore formed in weakly crosslinked systems when the rate of condensation conditions the gel structure can be highly compacted before it is sufficiently crosslinked to result in pore formation (Fig.4.4 a). For silica gels these conditional exist near the isoelectric point. Conversely low density gels are formed when ripening, neck growth and/or phase separation are promoted and the rate of condensation is high with respected to the rate of solvent removal. For silica gels these conditions are enhanced by increased water concentrations, intermediate pH 6-10 and elevated temperature.

There are numerous qualitative observations which support the concepts developed above. Brinker et al. prepared silica gels over a wide range of pH and water additions. No microstructural features were distinguishable in the highest density xerogels (ρ =1.63 g/cm³) while the lowest density xerogels (ρ =0.68 g/cm³) prepared at pH 8.8 were distinctly globular (21). Since at the gel point the acid catalyzed gels were composed of polymeric clusters, these microstructural observations suggest that phase separation was suppressed in the acid system, whereas the globular features observed in the base system may present the desiccated form of the original polymeric clusters or a desiccated, phase-separated structure.

Brinker and Sherer prepared multi-component silicate gels with three levels of both pH and H₂O. The highest density xerogels (ρ =127 g/cm³) were obtained at pH 2.5 (near the isoelectric point of silica). Aging these same gels for 3 weeks in 3M NH₄ OH solution prior to desiccation restructed the gel (presumably by ripening and neck formation) causing the desiccated gel (xerogel) density to decrease to 0.72 g/cm³ (25).

Reinforcement is most commonly carried out without much change of the gel structure by heat-aging the wet gel to an optimum degree. When carried further the aging process coarsens the structure. Depending on the character of the initial gel and the temperature, time and pH of aging, the gel structure can go through the states shown in Figure 4.10. Figure 4.10 A, gel as formed and dried. Shrinks on drying, giving small pore volume and small pore diameter. B, wet heat-aged-increased coalescence. Little shrinkage on drying. Pore diameter larger than dried A. C, furthers heat-aged or autoclaved. Structure coarsened: smaller area and larger pores but same pore volume as B. D disintegration to irregular rounded particles (68).



Figure 4.10. Stages in aging of gel. (68).



Figure 4.11. Electron micrograph of silica gel corresponding to stage B of Figure 4.10 (68).

The aging mechanism is simply the dissolving of silica from gel structure of smaller radios and deposition of silica on the larger or thicker regions. This mechanism was clearly described by Alexander, Broge, Iler (68).

It must be understood that the simple step of washing salts out of a gel is also an "ageing" step and the pH of the wash water is critical in the case of gels made from acid and silicate. Also, the final properties of such gels depend on both the pH at which the gel was formed and the pH at which it was washed (aged) before drying (68).

4.6 Drying of Xerogels and Membranes

The final porous microstructure in xerogels and membranes are established during drying. it is also very crucial because cracks tend to form during drying and this usually necessitates very slow controlled drying rates and processes. (15,21).

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 or xerogel. This is turn depends on a balance between the capillary pressures that tries to collapse the gel and stiffness of the gel that opposes it. For bulk gels this may take a lot longer (hours or days) than films (seconds or minutes) causing lower levels of condensation reactions in films during drying. Thus, capillary tension is higher causing greater collapse of the network in films. In summary films have lower pore sizes, pore volumes and surface areas than their bulk counterparts.

The stages of drying are illustrated schematically in Fig 4.12. Initially the gel consists of a continuos liquid phase. When evaporation begin to expose the solid phase, the liquid tends to spread over it, because the solid / vapor interface has a higher energy (γ_{SU}) than the solid / liquid interface (γ_{SC}). As the liquid stretches to cover the solid tensile stress appears in the liquid stretches to cover the solid tensile stress appears in the liquid and compressive stress is imposed on the solid network. The gel network is so compliant that it collapses into the liquid so that the network shrinks as fast as liquid evaporates, and the liquid / vapor meniscus remains at the exterior surface of the gel (Fig 4.12) (70). Figure 4.10 represent A) before evaporation begins, the meniscus is flat. B) capillary tension develops in liquid as it stretches to prevent exposure of the solid phase, and

network is drawn back into liquid. The network is initially so compliant that little stress is needed to keep is submerged, so the tension in the liquid is low and radius of the meniscus is large. As the network stiffens, the tension rises and, at the critical point (end of the constant rate period), the radius of the meniscus drops to equal the pore radius. C) during the falling rate period, the liquid recedes into the gel



Minimum radius of curvature

 $P_E = P_R$

Figure 4.12.Schematic illustration of drying process: black network represents solid phase and shaded area is liquid filling pores. (70).

During this stage, the curvature of the interface is relatively small and the evaporation occurs as if from a free liquid surface. This is known to clay technologies as the "constant rate period"; for gels, the drying time for a plate 5mm thick is typically a week to a month.

As the gel shrinks, its stiffness increases, because the solid network (whether it is particles or polymers) is becoming more tightly packed and because the aging process is occurring concurrently. As the gel stiffens, the pressure at the surface of the liquid rises until the meniscus reaches its maximum curvature (corresponding to the radius of the pore) and the full capillary pressure is imposed on the solid phase. When the gel is too stiff to contract under that pressure, shrinkage stops; in clay, this is known as the "leatherhead point". The amount of shrinkage that occurs up to that point depends on the amount of aging; in fact, very slow drying leads to higher pore volume, presumably because of more extensive aging during drying (70).

It is the shrinkage of the solid network at the critical point that establishes the final pore volume, pore size and surface area of the dry gel or xerogel. Therefore many strategies designed to tailor the porosity of either bulk or thin film xerogels rely on controlling the extent of shrinkage. The extent of drying shrinkage depends on the balance between the magnitude of the capillary pressure that collapses the gel and the stiffness of the gel that provides resistance to collapse. This balance depends in turn on the characteristic time scale of the drying process. For bulk gels, lying pathways for flow and diffusion require drying to occur slowly (hours to days), especially if cracking is to be avoided. For films, vigorous evaporation overlaps the complete deposition process. Within seconds the entrained sol is concentrated and dried to form an extremely thin solid film (typically 10 to 300 nm). This short characteristic time of the thin film deposition process represents the time for continued condensation reaction to occur. Thus, compared to bulk gels, films are less highly condensed prior to the critical point and hence suffer great collapse during drying. This has the synergetic effect of reducing the pore size, increasing P and greater collapse of the network. Consequently, films are characterized by lower pore sizes, pore volumes and surface areas than bulk counter parts (21).

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Drying process is composed of two successive stages. In the first stage, which is called 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:

 $P=2\gamma LV \cos\theta / r_p$

(14)

where ;

γLV: Liquid - vapor interfacial energy

 θ = Contact angle

 $r_p = Pore radius$

For wetting pore fluids ($\theta < 90^{\circ}$) the meniscus is concave and the liquid is in tension (positive P). The reduced volume of liquid stretches to cover the solid surface so that the creation of the higher-energy solid-vapour interfaces is avoided.

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 (70).

Obviously, using a solvent with a lower surface tension will reduce the capillary pressure. Smith and co- workers demonstrated this approach by aging silica gels in either ethanol or water and subsequently washing them in various aprotic solvents with a range of surface tensions. They found that for base catalysed gels, an increase in surface tension leads to a linear decrease in the surface area, pore volume, and pore size of dried samples. For acid catalyzed gels that are less highly cross-linked, the micropore surface area and pore volume increase with increasing surface tension, whereas total surface area and pore volume showed an opposite trend. These results clearly show the effects of network rigidity and capillary pressure on the microstructure of xerogels. Furthermore, they establish the feasibility of preparing high-surface area, low density materials at ambient pressure, in contrast with the preparation of aerogels with supercritical drying (21).

When (as is often the case) liquid evaporates only from one surface of a porous plate, capillary tension develops first on the drying surface. The tension draws liquid from the other surface in an effort to produce uniform hydrostatic pressure. If the permeability is high, the flux of evaporating liquid is readily provided with small pressure gradient. However, if the permeability is low or the plate is thick, the tension in the liquid can be greater on one face than on the other, and the compressive forces on the solid network will vary correspondingly. This situation is illustrated in photo of a piece of silica gel drying by evaporation from the upper surface. The low permeability of the gel leads to the development of a significant pressure gradient, so the network is subject to greater compression on the drying surface, and this causes it to wrap upward. At a later stage of drying, the liquid has retreated into the gel, so the pores near the upper surface are filled with air, and the surrounding network is released from compressive forces. However, the lower portion of the plate still contains liquid and that portion of the network is being compressed, so the direction of wrapping reverses (69).



Figure 4.13. Theory of drying (70).

Even though these adjacent interconnected pores have different radii (r_L) and r_S), liquid evaporates from them at the some rate, so the radii of the menisci (r_m) in the pores are equal during the constant rate period. As shown in Figure 4.13 if the radii were different the capillary tension 2 γLv / r_m would also be different liquid would flow from one pore to the other until the menisci become equal again. This sketch shows the critical point for the larger pore, when then radious of the pore ($r_m = r_L$). Unless it prevent by shrinkage of the solid network, further evaporation will force the liquid to retreat into the larger pore; however, r_m can continue to decrease in the smaller pore and the greater tension in the liquid in that pore will suck liquid from the larger pore. In this way, larger pores empty while smaller pores remain full of liquid (70).

This process can cause the liquid / vapor interface to move into a drying body in a highly erratic fashion. Figure 4.13 show the drying front moving through a bed of submicrometer silica spheres, the white regions in the Figure 4.3 are water-filled and the black regions in the photo are air-filled pores which scatter light. Low magnification shows that the boundary is atomically rough. Because of variations in pore size, regions containing thousands of pores can empty while the surrounding pores remain full. These dried pockets can cause scattering, making a drying body appear translucent or even milky white, even though individual pores are much too small to cause scattering. This phenomenon is obvious during the drying of porous Vycor glass, where the pores are smaller than 10 nm; the glass is perfectly transparent when fully wet or fully dry but turns white and opaque during drying (68).

It has been argued that cracking result from the variation of pore sizes in the gel, because the higher capillary pressure in a smaller pore could fracture the wall separating it from a neighbouring larger pore, as shown in Figure 4.12.

Aging helps to reduce cracking of gels, but it is still necessary to dry very slowly to avoid cracking of any macroscopic piece. Several much more efficient approaches have been suggested, including surfactants " drying control chemical additives (DCCA)", hypercritical drying and analysis. Since differential strain arises from capillary pressure, it's evident that surfactants can reduce the stress by reducing the interfacial energy. This is illustrated in Fig. 4.12.c, which shows much less acoustic activity (cracking) when a surfactant is added to the sol. Hypercritical drying eliminates the liquid/ vapor interface by heating the gel under pressure to a point above the critical temperature and pressure of the solvent.

At that point there is no difference between the solid / vapor and solid / liquid interfaces; that is, there is no capillary pressure. The hypercritical dried gel (called an aerogel) has the same volume as the sol from which it was made, because no compressive stress is applied to the solid phase during drying. If an aerogel is re-wet and dried, it collapses into the structure obtained by conventional drying. Although this method is extremely successful for silica gels, some compositions will dissolve in the aggressive environment of the autoclave (critical point of methanol is 240 $^{\circ}$ C and 78.5 atm.) (69).

Most supercritical drying is done with alcohol because of its use as a solvent in the sol-gel step. However, Tewari and Hunt showed that carbon dioxide can be used as a drying agent after the displacement of alcohol. There have been recent reports on the effect of drying agent (i.e.; alcohol versus carbon dioxide) on the properties of silica and titania-silica aerogels. Specifically, Smith et al. found that the surface area of a base - catalysed silica gel dried with carbon dioxide is about 25 % higher than that of a sample dried with ethanol. Because ethanol has a higher critical temperature than carbon dioxide, these authors ascribed this difference in surface area to accelerated aging at the higher temperature with alcohol facilitates the crystallisation of titania in titania-silica gels.

4.6.1 The use of DCCA's in Drying Processes

Organic additions called drying control chemical additives (DCCA) can be used for controlling sol-gel derived gel membrane monolith fabrication and drying to prevent cracking problems. These additives can control the rate of hydrolysis- polymerisation reactions, reduce drying stresses, and effect the pore size distributions. Organic like formamide, glycerol, oxalic acid, PVA and others are known to be used for this purpose (24).

The use of formamide was reported to reduce the gelation, aging and drying times, drying stress and increase the size of the gel monoliths in the preparation of SiO_2 gels from alkoxides. The formation of uniform particle sizes during sol formation and more uniform pore size distributions during drying are enhanced by the use of DCCA's. The DCCA's however must be removed during drying- calcination- densification before pore closure happens.

The term DCCA has been applied to a number of substances including glycerol, formamide and oxalic acid. Use of the formamide DCCA, compared with methanol alone, leads to a larger gel network. Consequently, a larger pore size distribution is developed in the gel but still with a narrow distribution of pores. The gel network has substantially larger necks and greater strength. Therefore, large silica gel monoliths made with formamide DCCA's can be dried much more rapidly without cracking. Use of oxalic acid as DCCA also controls the size and shape of the pore distribution curve.

Either formamide or the organic acid DCCA greatly decreases the breadth of the pore distribution, which decreases the magnitude of capillary stresses induced during drying. The above results suggest the mechanisms for DCCA control of silica sol-gel processing as depicted schematically in Fig. 4.14- 4.17. Fig. 4.14 illustrates the sequence of structural changes that must be controlled in order to produce large scale monoliths with a range of densities (24).





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Either formamide or the organic acid DCCA greatly decreases the breadth of the pore distribution, which decreases the magnitude of capillary stresses induced during drying. The above results suggest the mechanisms for DCCA control of silica sol-gel processing as depicted schematically in Fig. 4.14- 4.17. Fig. 4.14 illustrates the sequence of structural changes that must be controlled in order to produce large scale monoliths with a range of densities (24).





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Addition of basic DCCA such as formamide produces a large sol-gel network with uniformly larger pores. An acid DCCA, such as oxalic acid, in contrast results in a somewhat smaller scale network after gelation but also with a narrow distribution of pores. Thus, either basic or acidic DCCA's can minimize differential drying stresses by minimizing differential rates of evaporation and ensuring a uniform thickness of the solid network that must resist the drying stress. Achieving a uniform scale of structure at gelation also results in uniform growth of the network during aging which thereby increases the strength of the gel and its ability to resist drying stresses. Recent work indicates that this ultrastructural control is due to the DCCA's effect on the rates of both hydrolysis and polycondensation as discussed above.



Figure 4.15. Control of sol-gel processing with organic acid DCCAs. Step1:Sol Formation

Without a DCCA a wide range of pore sizes and diameter of solid network are produced (Fig. 4.14 - 4.17) when gelation occurs. Differential growth of the silica network will thereby occur during aging due to local variations in solution-precipitation rates. The net effect is an aged gel structure such as depicted in Fig. 4.14-.17, with many regions susceptible to cracking during drying.



Figure 4.16. Step 2 and 3: Gelation and aging (24)

As shown in Step 5 in Figure 4.17 an effect of DCCA, however, must also be capable of being removed during densification before pore closure. The DCCA must also be capable of removal during drying without producing a residue, which is sensitive to moisture.



Figure 4.17. Step 4 and 5: Drying and densification (24)

X-Ray diffraction of the formamide DCCA silica gels showed no evidence of devitrification; however, FTIR analysis showed a 926 cm⁻¹ SiOH peak still present. The major problem in the formamide DCCA process is a tendency for residual formamide to react with water vapour. When the adsorption occurs preferentially on the surface of the dried gel uneven stresses develop. Therefore, it is essential to eliminate residual formamide without exposure to water vapour if full densification of monoliths is to be achieved (24).

In order to avoid the moisture related densification problems associated with the formamide DCCA, organic acid DCCAs have also been used with TMOS and H_2O to form large monolithic silica gels. The specific surface area of the fully dried silica gels made in this manner using oxalic acid DCCA is 690 m²/g prior to densification with an average pore size of only 20 A°. The tail of the pore size distribution does not exceed 70 A° which accounts for the excellent optical transparency of these silica monolithics.





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There is a little change in the pore size distribution of the DCCA silica gels until densification occurs at T> 600 $^{\circ}$ C, Fig 4.18. The most interesting feature of densification of these gels is that the mesopores are eliminated first and subsequent densification occurs with the mean pore size remaining small. Densification primarily is due to only the number of pores decreasing.

The silica gel monolithics made with an oxalic acid DCCA show a broad range of physical properties depending upon densification temperature, while optical transparency is maintained throughout.

By varying the densification temperature it is possible to obtain an index of refraction of silica matrix between n= 1.397(at λ =0.6328 µm) and that of dense vitreous silica, n=1.457. This makes it possible to produce silica lenses of very low index of refraction when the microporosity is taken into account. If we assume the same dispersion reported by Malitson for vitreous silica, these gels-derived silicas provide a family of optical components with properties not previously available from melt-derived process. With the exception of the lowest temperature samples (150^oC) this wide range of n is achieved sacrifice of the IR absorption edge.

For certain applications, an important feature of the sol-gel silica derived silica lenses is their low density. A sol-gel silica lens densified at 750 0 C is environmentally stable and half the strength of vitreous silica and only 61 % of the density. Thus, large lenses will have substantially lower weight requiring less support structure, and so on.

As a result, the shrinkage of the gel is uniform (i,e, there is less differential strain), so warping and drying stresses are minimized. The later phenomenon may account for the success of the osmotic extraction procedure discovered by Yoldas, the sol is placed in to a dialysis membrane and immersed into alcohol (or salt solution); the water diffuses out of the sol producing gelation followed by accelerated shrinkage. In this way an alumina gel to shrink to the leatherhead point in a matter of hours. Since the water in alcohol within the gel, so the water can be extracted from the interior of the gel with a minimum of differential strain. It should be noted that DCCAs can be very difficult to remove after drying, so that sintering is difficult or impossible, while the dialysis method does not introduced any contaminant into the gel. (69)

4.7 Ceramic Membrane Support Type and Their Preparation

The fabrication of polycrystalline technical ceramics generally involves the consolidation and shaping of a fine powder, followed by a sintering process to achieve the requisite fired microstructure and properties. Two important methods for achieving these steps in the manufacturing of refractory and electronic technical ceramic components are dry pressing and slipcasting (39,40).

Dry pressing may be defined as the simultaneous uniaxial compaction and shaping of a granular powder with small amounts of water and/or organic binders during confined compression in a die. The extensive particle of dry pressing stems from the inherent ability to form rapidly a wide variety of shapes with close tolerances and controlled compact character using highly mechanised and automated equipment. For example, steatite's, alumina's, titanates, and ferrites have been dry pressed in sizes ranging from a few mils to several inches in linear dimensions at rates up to 5000 parts per minute on smaller parts. The force of dry pressing is the manufacture of small parts with surface relief in the pressing directions. Sheets of ceramic with high aspect ratios, less than a few hundred mils thick, are now conventionally formed by continuous tape casting; and for shapes with one greatly elongated dimension or with two - or three- dimensional surface relief, other fabrication methods such as extrusion and slipcasting can be competitive (39).

A squence of intermittent steps is involved in dry pressing a ceramic component. Feeding is typically synchronised with a drop in the bottom piston followed by a compression step and then ejection of the piece. For soft powders the die materials are typically abrasion - resistant hardened steels with a Young's modulus of elasticity. For longer wear or abrasive powders, special steel, boride steel, or metal carbide tooling is employed. Pressures range up to several tens of thousands of psi; punch speeds are of the order of a fraction to a few seconds Functional variables which must be considered in the press design are : 1) design of die set (geometry, materials, gap between movable and fixed components; 2) powder feed mechanism and driving force for filling; 3) flow and compaction properties of powder (control character); 4) temperature and atmosphere of feed powder and die; 5) punch pressure and/or displacement program and dwell time and ; 6) ejection program. Accordingly, the press must be equipped to provide the requisite actions with sufficient precision to ensure reproducible compact character and geometry (39).
Slipcasting is a unique process that the ceramist has long utilised as one of his basic forming techniques. It is a very versatile process- one that is based both by the ceramic artist and manufacturer of highly sophisticated technical ceramics. The versatility of the process has led to development of slip casting techniques for many different materials.

In essence, slip casting consists of the following steps;

1) Preparation of a mixture of a powdered material and liquid into a table suspension called a slip.

2) Pouring this slip into a porous mold, usually made from plaster of paris, and allowing the liquid portion of slip to be partially absorbed by the mold. A layer of semihard material is formed against the mold surface as liquid is removed from the slip.

3) Interrupting the casting process when a suitable wall thickness has been formed. This is known as drain casting. Alternatively, a solid object may be made by allowing casting to continue until the entire mold cavity is filled with semihard material. This variation is called solid casting.

4) Drying the material in the mold to provide adequate strength for handling. Some shrinkage usually occurs in this step.

5) Removal of the solid object from the mold.

The slip cast article has sufficient strength to be handled and to permit other operations such as trimming rough surface from mold seams. Ware made by slip casting is rarely used in this form but is subsequently fired at a temperature suitable for densifying the particles into a cohesive structure. The firing operation is much like that used in other ceramic processing (40)

There are many advantages of slip casting. It is ideally suited for forming thinwalled and complex shapes of uniform wall thickness. The molds, being made from plaster of Paris, are inexpensive. This feature makes slip casting especially attractive for development items or short productions. The primary disadvantages of the process are its lack of precise dimensional control (40).

4.8 Heat Treatment of Xerogels and Membranes

Phase formation and/or grain growth can occur at different temperature for the currently used membrane materials like SiO₂, Al₂O₃, TiO₂, ZrO₂, etc. The membranes will become sinteractive at around 500-600 °C for TiO₂, 900-1000 °C for ZrO₂, 300-400 °C for SiO₂ and number of phase transformations will occur for Al₂O₃ in the 500-1200 °C range. Initial stage sintering usually will coarsen the grains and increase the pore size and density of the structure. The variation of pore size with temperature was shown to vary from 3 nm to 55 nm in the 400-1200 °C range (5,37). Doping the boehmite sol with lanthanum nitrate and PVA was observed to stabilise the structure thermally at even 1100 °C (18,19,22).

CHAPTER 5

CHARACTERIZATION OF INORGANIC MEMBRANES

The separation efficiency (e.g. permselectivity and permeability) of inorganic membranes depends, to a large extent, on the microstructural features of the membrane/support composites such as pore size and its distribution, pore shape, porosity and tortuosity. The microstructures and the membrane/ support geometry will be described in some detail particularly for commercial inorganic membranes. Other material related membrane properties will be taken into consideration for specific separation applications. For example, the issues of chemical resistance and surface interaction of the membrane material and the physical nature of the module packing materials in relation to them embrowns will be addressed. (1)

Some commercial inorganic membranes have a symmetric or homogenous microstructure. However, the majority of the commercially important inorganic membranes are asymmetric and composite in nature. They usually consist of a thin fine pore film responsible for separating components and a support or substrate with single or multiple layers having larger pores for improving the required mechanical strength to the membrane composite.

The basic idea behind the composite and asymmetric structure is to minimise the overall hydraulic resistance of the permeate flow path through the membrane structure. The permeate flux through a given layer is inversely proportional to some power of the pore size of the porous layer.

The final properties of ceramics are their microstructure and also their most important mechanical, thermal, electrical, chemical properties strongly depend on the physical and chemical properties of the starting powders. The most important physical properties of ceramic powders are specific surface areas, primary particle sizes, agglomerate sizes, their unfired compacts, and the morphology of the particles. The chemical composition and the nature of the phases are also very important. This section will cover the pore size determination and thermal morphological characterization techniques briefly since these are very important for ceramic membrane performance. FTIR and XRD can be used as determination of structural properties, TGA, DTA, DSC can be used to determine thermal properties, gravimetric or volumetric adsorption system can be used for determination of adsorption related properties.

5.1 Determination of Pore Size Distributions

The following classification is usually made about the types of pores present in porous materials. Pores with diameters larger than 50 nm are called as macropores, mesopores have diameters between 2-50 nm, and pores below a diameter of 2nm are called as micropores. This classification also fits to the pore size determination techniques commonly used. Optical microscopy is limited to relatively big Macropores, Mercury porosimetry is limited with Macropores and Mesopores and low temperature gas adsorption and desorption are mainly limited to Micropores and Mesopores.

The physical adsorption of gases by solids increases with decreasing temperature and with increasing pressure. The process is exothermic, i.e., energy is released. The kinetics and thermodynamics of adsorption have been extensively studied, but, when surface area and pore structure are the subjects of interest, the investigative procedure is first to establish what is known as an adsorption (or desorption) isotherm. This, quite simply, is a measure of the molar quantity of gas n (or standard volume Va, or general quantity q) taken up, or released, at a constant temperature T by an initially clean solid surface as a function of gas pressure P. Most frequently the test is conducted at a cryogenic temperature, usually that of liquid nitrogen (LN2) at its boiling point (77.35 K at one atmospheric pressure). Convention has established that the quantity of gas adsorbed is expressed as its volume at standard conditions of temperature and pressure (0 C and 760 torr and signified by STP) while the pressure is expressed as a relative pressure which is actual gas pressure P divided by the vapor pressure Po of the adsorbing gas (called the adsorptive prior to adsorption and adsorbate afterward) at the temperature at which the test is conducted. Regardless of how the data are obtained and how manipulated thereafter, all analyses first must establish information in the form of quantity adsorbed (or desorbed) vs. Pressure; therefore the requirement that these measurements be of the highest quality cannot be overemphasized. These data, having been gathered at one temperature, constitute the adsorption (desorption) isotherm for the material in question. Plots of Va as the ordinate against P/Po as the abscissa reveal

much about the structure of the adsorbing the following material called the adsorbent) simply from their shape.

Adsorption isotherms generally follow one of six forms, the first five of which originally were assigned type numbers by Brunauer. The sixth is a recent addition; all are produced here in Figure 5.1.

Type I isotherms are encountered when adsorption is limited to, at most only few molecular layers. This condition is encountered in chemisorption where the asymptotic approach to a limiting quantity indicates that all of the surface sites are occupied. In the case of physical adsorption, type I isotherms are encountered with microporous powders whose pore size does not exceed a few adsorbate molecular diameters. A gas molecule, when inside pores of these small dimensions, encounters the overlapping potential from the pore walls which enhanced the quantity of gas adsorbed at low relative pressures. At higher pressures, the pores are filled by adsorbed or condensed adsorbate leading to plateau, indicating little or no additional adsorption after the micropores have been filled. Physical adsorption that produced the type I isotherm indicates that the pores are microporous and that the exposed surfece resides almost exclusively within the micropores, which once filled with adsorbate, leave little or no external surface or additional adsorption.

Type II isotherms are most frequently encountered when adsorption occurs on nonporous powders or on powders with pore diameters larger than micropores. The inflection point or knee of the isotherm usually occurs near the completion of the first adsorbed monolayer and with increasing relative pressure, second and higher layers are completed until at saturation the v-number of adsorbed layers become infinite.

Type III isotherms are characterized principally by heats of adsorption which are less than the adsorbate heat of liquefaction. Thus, as adsorption proceeds, additional adsorption is facilitated because the adsorbate interaction with an adsorbed layer is greater than the interaction with the adsorbent surface.

Type IV isotherms occur on porous adsorbent's possessing pores in the radius range of approximately 15-1000 A°. The slope increase at higher elevated pressures indicates an increased uptake of adsorbate as the pores are being filled. As is true for the Type II isotherms, the knee of the Type IV isotherm generally occurs near the completion of the first monolayer.



Figure 5.1. The six basic adsorption isotherms types (70).

Type V isotherms result from small adsorbate-adsorbent interaction potential similar to type III isotherms. However, type V isotherms are also associated with pores in the same range as those of the type IV isotherms.

Type VI isotherms, indicative of a nonporous solid with an almost completely uniform surface, is quite rare. Only isotherm Types I,II and IV will be encountered here.

An adsorption isotherm for a hypothetical, completely nonporous material Figure 5.2, rises comparatively rapidly at low relative pressures, rises only moderately at intermediate relative pressures, and then rises quite rapidly as the relative pressure approaches unity. Reversing the procedure by reducing the relative pressure leads to a retracing of the curve. The initial rise in the curves is due to adsorbing molecules interacting first with the most energetic regions of the solid surface and then with the less energetic regions. As these regions are occupied the rise of the curve diminishes. By the midpoint of the curve, attachment of additional gas molecules on sites already occupied is occurring, i.e., additional layers are forming. The abrupt rise at the end is due to the adsorbing gas beginning bulk condensation to a liquid. Surface area information resides in lower region of the curve.



Figure 5.2. Adsorption and desorption isotherms for a nonporous solid.



Figure 5.3. Adsorption and desorption isotherms for a porous solid.

The adsorption curve of Figure 5.3 has the same general shapes as that of Figure 5.2 except that it rises more rapidly in the intermediate zone and shows a wide hysteresis loop instead of nearly retracting the adsorption curve. This behaviour is typical of mesoporous and macroporous materials, i.e., those that have pores with openings greater than 2nm and 50 nm respectively. Such pores are likely to have a wide range of sizes and shapes. They also may interconnected with one another.

Adsorptive molecules to two walls of a pore experience enhanced attractive forces. These forces lead to the beginning of gas condensation at lower relative pressure than in the case of a nonporous solid, and pore filling with multilayers of adsorptive molecules and then with condensate accounts for the rise of the middle part of the curve.

The occurrence of a wider, more-pronounced hysteresis loop indicates that evaporation from a pore is a distinctly different process from condensation with it. When gas condenses in a pore, as illustrated in Figure 5.4, the condensate builds from the walls inward toward a central core decreasing diameter. However, it must evaporate from a liquid surface with a quite different curvature. This inhibits the evaporation and causes the decreasing portion of the loop to lag behind until all pores have emptied. Adsorbent surface area and pore geometry are intimately intertwined in this type of material. Analysis of essentially the entire curve is required to external all its information.



Figure 5.4. Condensation in and evaporation from a pore open at both ends.

It should be noted that the absence of a hysteresis loop as in Figure 5.2 is not conclusive evidence of nonporosity. Certain conical, edge and closed-end pore geometry can yield isotherms without hysteresis.

The hysteresis loops of some isotherms are closed in the pressure region near saturation as illustrated in Figure 5.5. This shape reveals that the adsorbing solid contains mesopores with an upper size restriction.

The adsorption isotherm is quite different when the adsorbing solid contains only microspores, pores less than about 20 Å in width. The extraordinary adsorption capacity of such materials is not a surface phenomenon but is due to enchanted adsorption in microspores. A microporous material isotherm, Figure 5.6, plotted to the same scale as the previous isotherms shows the curve to rise almost vertically, level out to a long, nearly horizontal section, and then to rise as saturation is approached and bulk condensation begins to occur. Examined in greater detail, the initial rise is not precipitous. What it reveals is that adsorption takes place by micropore filling and the progressively larger micropores fill in order of increasing size, albeit under a driving force of quite low relative pressure. Once the micropores have filled, very little adsorption takes place thereafter for there is essentially no place remaining on which adsorption can occur. There is no hysteresis save at near unity relative pressure, as in Figure 5.2. Typical materials of this types are zeolites and microporous carbon. They are proving to be exceptionally useful adsorbent's and catalysts.



Figure 5.5. Adsorption and desorption isotherms for a solid with limited pore size range.



Figure 5.6. Adsorption and desorption isotherms for a microporous solid. The inset shows the steep rising region of the plotted on a logarithmic x-axis.

The several isotherms are drawn to emphasise distinct characteristics, whereas actual materials can and do, have pores in all size ranges, pores restricted to two or more size intervals with few in between, and with various other proportions of pore size. Accordingly, isotherms shape vary enormously and detailed examination in accordance with thermodynamic and other principles is required to elicit the desired information of surface and pore structure.

5.1.1 Surface Area

B.E.T and Langmuir adsorption methods are most widely used procedures for the determination of the surface area of finely divided and porous materials.

5.1.1.1 B.E.T Model

The adsorption isotherm data may be used to calculate the surface area of the sample. The procedure known as the BET method was introduced by, Branauer, Emmett, and Teller. It is the most widely used procedure for the determination of surface area of finely divided and porous material. The B.E.T model is based on assumption that each molecule in the first adsorbed layer is considered to provide one site for the second and subsequent layers. The molecules in the second and subsequent layers, which are in contact with other sorbate molecules rather than with the surface of the adsorbent, are considered to behave essentially as the saturated liquid. In this manner the equilibrium constant for the first layer molecules in contact with the surface of the adsorbent is different. The linear BET equation in its most common from is given by:

P is the pressure, Po is the saturation pressure, Va is the quantity of gas adsorbed at pressure P, Vm is the quantity of gas adsorbed at monolayer

Classically, this equation was used for types II and IV isotherms only, but it may also be used for type I data, depending upon the C constant, which is related to the enthalpy of adsorption. In practice, the value of C can be used to define the measure of heat of adsorption. A high value of C (\cong 100) is associated with a sharp knee in the isotherm. If C value is low (<20) the sharp knee cannot be identified as a single point in the isotherm.

5.1.1.2 Langmuir Model

Langmuir was the first to propose a theoretical equation relating the quantity of adsorbed gas to the equilibrium pressure of the gas. The Langmuir model was originally developed to represent chemisorption on a set on a distinct localized adsorption sites. The basic assumptions on which the model is based on are as follows;

Molecules are adsorbed at a fixed number of well-defined localized sites. Each site can hold one adsorbate molecule. All sites are energetically equal. There is no interaction between molecules adsorbed on neighbouring sites.

 $\frac{P}{V} = \frac{1}{bVm} + \frac{P}{Vm} \tag{2}$

Where;

P is the pressure, Po is the saturation pressure, Va is the quantity of gas adsorbed at pressure P, Vm is the quantity of gas adsorbed at monolayer, b is the empirical constant

5.1.2 Characterization of Micropores : Pore Size Distribution

MP, Dubinin-Radushkevich, Dubinin-Astakhov and Horvath-Kawazoe methods are the evaluated mathematical models for pore size distribution.

5.1.2.1 MP Method

Mikhail et al. proposed a method for constructing pore size distribution from the t-plot. The t-plot is a plot of t, the statistical thickness, versus the relative pressure, P/Po. The t-plot employs a composite t-curve obtained from the data on number of nonporous adsorbents with BET equation C constants similar to those of the microporous sample being tested. The standard t-curve is expressed by the empirical de Boer equation .

5.1.2.2 Dubinin-Raduskevich and Dubinin-Astackhov Methods

The second means of determining PSDs of microporous materials from gas adsorption measurements is based on the theory of volume filling of micropores. The theory of filling of micropores (TVFM) is applied most widely for describing the physical adsorption of gases and vapours in micropores. This theory is based on the assumption that the characterization adsorption equation is expressing the distribution of the degree of filling of the adsorption space. This theory incorporates earlier work by Polanyi in regard to the adsorption potential.

5.1.2.3 HK Method

The Horvath – Kawazoe method was developed to determine the effective pore diameters of microporous solids (solids with pore diameters smaller than 20 A). The authors to molecular sieve carbons applied the method, but Venaro and Chiou and Seifert and Enig have extended it to zeolite and other oxide-type microporous materials. 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.

$$RTD_{I}\left[\frac{P}{P_{O}}\right] = K\left[\frac{\left(N_{a}A_{a}+N_{A}A_{A}\right)}{\sigma(l-d)}\right] * \left[\frac{\sigma^{4}}{3\left(l-\frac{d}{2}\right)^{3}} - \frac{\sigma^{10}}{9\left(l-\frac{d}{2}\right)^{9}} - \frac{\sigma^{4}}{3\left(\frac{d}{2}\right)^{3}} + \frac{\sigma^{10}}{9\left(\frac{d}{2}\right)^{9}}\right] \dots \dots \dots \dots (3)$$

where;

Na the number of atoms per unit area of adsorbent

NA the number of the molecules per unit area of adsorbate

Aa & AA are constants in Lennard-Jones potential for adsorbent & adsorbate

 σ is the distance between a gas atom and the nuclei of the surface at zero interaction energy.

5.1.3 Characterization of Macro-Mesopores

The Kelvin equation, BJH adsorption and desorption method are used in the characterization of the mesoporous and macroporous materials.

5.1.3.1 Kelvin Equation

In porous adsorbent there is continuous progression from multilayer adsorption to capillary condensation in which the smaller pores become completely filled with liquid sorbate. This occurs because the saturation vapor pressure in a small pore is reduced by the effect of surface tension.

The mesopore size is usually calculated with the aid of the Kelvin equation in the form.

$$Ln\frac{P^*}{Po} = -\left[\frac{2\gamma * vCos\theta}{RTr_m}\right].$$
(4)

where;

 P^* is the critical condensation pressure, γ is the liquid surface tension θ is the contact angle between the solid and the condensed phase r_m the mean radius of the curvature of temperature liquid meniscus

5.1.3.2 BJH Method

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 is likewise decreased. The mathematics of the technique is equally applicable whether following the adsorption branch of the isotherm from high to low pressure or the desorption branch.

5.2 FTIR (Frouer Transform Infra-Red)

Vibrational spectroscopy in another name 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.

5.3 Thermal Analysis Methods

The thermal stability of ceramic precursor and membrane materials can best be studied by Thermogravimetric (TGA) and Differential Thermal Analyser (DTA). The decrease or increase in the weight of a sample is followed as the temperature is slowly increased up to 1000 °C in TGA. The information can be very valuable in the determination of the optimum calcination temperature above information and the phase stability. The optimum heat treatment conditions further should be determined by using pore size distribution information and SEM pictures. The microstructures of ceramic membranes may drastically change due to sintering above certain temperatures

5.4 Microstructure Analysis by Electron Microscopy

Scanning Electron Microscopy (SEM) and Optical Microscopy can be used for the morphological-microstructure characterization of ceramic membranes. SEM is a versatile technique in which 5-50 keV electron beam scans the specimen surface. The resulting secondary electrons, X-rays and backscattered electrons are detected and analysed to form images. Magnifications up to 100.000 can be obtained. The morphology of the ceramic particles making up the membrane, their packing, and the resulting pore structure can be analysed. Low magnification possibly present these materials.

Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and nitrogen adsorption / desorption isotherm analyses were used to characterise the physical structure of the desiccated gel. For both SEM and TEM the gels are first heated to 250 °C which was the degassing temperature employed for the nitrogen sorption analyses.

A scanning electron microscope (SEM) generates electron beams and forms an image from the emitted electrons as a result of interaction between the bombarding electrons and the atoms of the specimen. Since electrons have a much shorter wavelength than light photons, SEM' s can generate higher resolution information than reflected light microscopes. With their improved resolution and competitive pricing, SEM s have become a basic surface and microstructural characterisation tool in membrane separations. This is particularly true for porous materials such as porous inorganic membranes where the three-dimensional appearance of textured surfaces can be revealed by the depth - of field feature of a SEM.

5.5 Microstructure Analysis by Atomic Force Microscopy

Atomic force microscopy (AFM) images show critical information about surface feature with unprecedented clarity. The AFM can examine any rigid surface, either in air or with the specimen immersed in a liquid. "Minor" (and major) differences between "smooth" surfaces are shown dramatically. On one hand, the AFM can resolve very tiny features, even single atoms, that were previously unseen. On the other hand, the AFM can examine a field of view larger than 125 microns (0.005 inch), so that you can make comparisons with other information, e.g. features seen in the light microscope or hazes seen by eye. The AFM can also examine rough surfaces, since its vertical range is more than 5 microns.

Large samples fit directly in the microscope without cutting.AFM can easily examine any area on flat specimens up to 8" (20 cm) in diameter and up to 0.5" (12.7 mm) thick.

A tiny tip gently contacts the specimen. As the XYZ translator scans either the specimen or the tip horizontally in a raster pattern (XY), the stylus rides up and down the surface hills and valleys. The deflection of the tip is registered by the laser/photodiode sensor and the XYZ translator adjusts tip or specimen (depending on microscope) up or down (Z) to restore the tip to its original orientation. The computer stores the vertical position at each point and assembles the image.

For image display, the vertical (Z) and horizontal (XY) ranges independently, to best present the surface structure. Using "dual magnification," the AFM combines the wide field view of a Scanning Electron Microscope (SEM) with vertical resolution which exceeds that of a Transmission Electron Microscope (TEM). The ratio of the vertical to horizontal magnification can be very large (1000 or more) to allow easy perception of differences between very smooth surfaces.



Figure 5.7. AFM images of surface features of coating.

Topographic results can be enhanced by simultaneously using other modes of AFM data capture, such as phase imaging. In Figure 5.7 (a), we see the many interesting surface features of the coating. When combined with the phase image in Figure 5.7 (b), we can now tell which features are of similar chemical composition. This allows determining whether surface features may be the result of a residue or specific chemical component, or whether the surface is homogeneous.

In addition to its superior resolution, the AFM has these key advantages:

Compared with Scanning Electron Microscopes (SEM), the AFM provides extraordinary topographic contrast, direct height measurements and unobscured views of surface features (no coating is necessary).

Compared with Transmission Electron Microscopes, 3-dimensional AFM images are obtained without expensive sample preparation and yield far more complete information than the 2-dimensional profiles available from cross-sectioned samples.

Compared with Optical Interferometric Microscopes (Optical Profilers), the AFM provides unambiguous measurement of step heights, independent of reflectivity differences between materials.



(a)

(b)

Figure 5.8. AFM images of the bulk surface.

Another mode of operation which can be useful when combined with topography is friction imaging. In the height image in Figure 5.8 (a), there are several areas where the topography appears higher and rougher than the bulk surface. When combined with a friction image in Figure 5.8 (b) we see that there is a contaminant on the surface which appears dark in the image. Therefore the contaminant has a lower coefficient of friction than the underlying surface. This can be helpful in determining the source of the contaminant.

CHAPTER 6

EXPERIMENTAL

6.1 Materials

Alumina sols were prepared by using Aluminum Isopropoxide, 2-Propanol, Nitric acid and Water. Silica sols were prepared by using Tetraethylortosilicate (TEOS), Ethanol, Water, HNO₃ in predetermined ratios. The properties of these materials used in this work are tabulated in the Table 6.1. Membrane supports were prepared by using an α Al₂O₃ powder and PVA as binder.

Table 6.1 : Specifications of the Materials

Aluminum Isopropoxide [(CH ₃) ₂)CHO] ₃ Al	98%, M=204.2, d=1.035 Aldrich		
Tetraethylorthosilicate	98%, M=208.33, d=0.934		
$Si(OC_2H_5)_4$	Aldrich		
2-Propanol	99.5%, M=60.1, d=0.78		
CH ₃ CH(OH)CH ₃	Merck		
EthylAlcohol	99.8 %, M=46.07, d= 0.79 - 0.791		
C ₂ H ₆ O	Riedel		
Nitric Acid	65%, M=63.01, d=1.40		
HNO ₃	Merck		
Alumina Powder	99,99 %, BET = 12,3 m ² /g		
αAl_2O_3	Sumitomo (AKP-53)		
Polyvinyl alcohol	M=9000-10000, 80%		
IPVA			

6.2 Preparation of Sols

6.2.1 Alumina Sols

In this study twelve alumina sols were prepared. The compositions and the codes of the alumina sols are given in Table 6.2. In AlHO to AlH5 sols, Water/Alkoxide ratio were kept constant whereas H^+/Al^{3+} ratios changing within 0.1 to 0.6 respectively. And in Al1 to Al6 sols Water/Alkoxide ratios were increased within 200 to 100 since H^+/Al^{3+} ratio was kept constant.

Predetermined amount of Aluminum isopropoxide and 2-propanol were mixed for 2 hours at 80 °C. These solution had a yellowish color. And then water were heated up to 80 °C and added into the alkoxide-alcohol mixture and stirred 2,5 hours at 80 °C. These solution had a white gelatinous solution. Finally, nitric acid solution was added dropwise to these solutions. This sol mixture was kept for another 2 hours at 80°C under constant stirring. All the sol preparations were done in Pyrex shott bottles within opened caps. These sols were stored at room temperature in these bottles with closed caps.

16 grams of aluminum isopropoxide, 100ml 2-propanol, 11ml Nitric acid solution (1,44M, 10%) and 271ml water were used for Alh1 and Al1 sols.

Kod	H ⁺ /Al ³⁺	H ₂ O/Alkoxide	
AlHO	0.1	200	
AlH1	0.2	200	
AlH2	0.3	200	
AlH3	0.4	200	
AlH4	0.5	200	
AlH5	0.6	200	
Al1	0.2	200	
A12	0.2	180	
A13	0.2	160	
Al4	0.2	140	
A15	0.2	120	
Al6	0.2	100	

Table 6.2. Acid/alkoxide ratios and Water/Alkoxide ratios for Alumina sols.

6.2.2 Silica Sol

In this study fourteen types of silica sols were prepared from tetraethylortosilicate (TEOS). The composition and the codes of the silica sols are given Table 6.3. In SiA to Sil silica sols, Water/Alkoxide ratios were varied from 3 to 15 whereas Acid/ Alkoxide ratios were kept constant. In SiH1 to SiH4 sols, Acid/Alkoxide ratios were increased from 0.01 to 0.1 since Water/Alkoxide ratio was kept constant.

Predetermined amount of TEOS and Ethanol were mixed for 2 hours at 50 ± 5 °C. Water and nitric acid solution were heated up around 50 °C and then added dropwise to the TEOS, alcohol mixture. These sol mixtures were kept another 3 hours at 50 ± 5 °C. Finally clear silica sols were produced. All silica sols were prepared in Pyrex shott bottles within opened caps. These sols were stored at refrigerator. 223 ml TEOS, 60ml water, 59ml nitric acid and 154ml ethanol were mixed for preparation of SiE (SiH3) sol.

Kod	TEOS	Water	HNO ₃	Ethanol
SiA	1	3	0.085	3.8
SiB	1	4	0.085	3.8
SiC	1	5	0.085	3.8
SiD	1	6	0.085	3.8
SiE 1		6.4	0.085	3.8
SiF 1		7	0.085	3.8
SiG	1	8	0.085	3.8
SiH	1	9	0.085	3.8
SiJ	1	10	0.085	3.8
SiL	1	15	0.085	3.8
SiH1	1	6.4	0.01	3.8
SiH2	1	6.4	0.05	3.8
SiH3	1	6.4	0.085	3.8
SiH4	1	6.4	0.1	3.8

Table 6.3. Mol ratios of TEOS, Water, Nitric acid, and Ethanol for Silica sols.

6.3 Unsupported Ceramic Membranes Preparation

Unsupported membranes were prepared for characterization experiments. All silica and alumina sols have been dried in 88cm petri dishes.

Alumina sols have been taken 10 ml then dried under 25 °C, 1 day calcined at 600 °C, 3 hours, 4 °C/min heating and cooling rate. Silica sols have been taken 5 ml then dried under 25 °C 1 day. Then calcined at 400 °C, 3 hours, 4 °C/min heating and cooling rate. Heat treatment were done Carbolite RH 1600 programmable furnace.

6.4 Alumina Support Preparation

Alumina support discs were prepared from Sumitoma AKP-53 powder. These 100 grams of powder was mixed with PVA solution which is 3 grams PVA and 50 ml water, then dried until 3% relative humidity. Then 10 gr powder was taken and made a pellet at dry press. After pellet preparation, pellet was heat treated at 1100 °C, for 3 hours.

6.5 Membrane Preparation

The membranes were prepared the layered structure of the Al_2O_3 and SiO_2 . Alumina thin membrane layer was prepared by three dipping procedures on αAl_2O_3 support by using AlH1 (Al1) alumina sol. The standard dipping time for 1 dip was 4 seconds. After the dipping process membranes were calcined for 3 hours at 600 °C (heating and cooling rates of 4°C/min.

The silica active layer on two-alumina layer was prepared by two dipping procedures. In first dipping, silica SiE (SiH3) sols were diluted 10 times. Second dipping were performed by a sol which is 180 times dilute SiE sols. This dipping procedure is to repair possible pinholes and/or cracks. 4 seconds also the standard dipping time for SiO₂ layer, too. After dipping, this silica layered α - γ - alumina membranes were heat treated. 3 hours at 400°C (heating and cooling rates of 4 °C/min).

6.6 Characterization

The pore size distribution and pore area characterizations were performed in Volumetric adsorption-desorption analyzer (Micromeritics – ASAP 2010). Selected samples from alumina and silica unsupported membranes were characterized by Nitrogen and Argon adsorption -desorption experiments. About 0.1gr alumina unsupported membrane samples were degassed 1 hour at 90 °C and 4 hours at 350 °C then analyzed at Volumetric adsorption-desorption analyzer. About 0.1-gram silica unsupported membrane samples were degassed 1 hour at 90°C and 1 day at 350 °C then analyzed. Relative pressure, adsorptive gas (N_2 , Ar,...), dose amount were specified before starting the analysis.

Pore size calculation were performed according to cylindrical geometry BJH method for Alumina unsupported membranes. And pore size calculations were performed Horward-Kawazoe spherical geometry model for silica samples.

The TGA curves were archived by Thermal gravimetric Analyzer (TGA-51/51H, Shimadzu Co.) The carrier gas was Nitrogen at a flowrate of 15 ml/min and the heating rate is 10 C/min. The FTIR Spectrum was achieved by Fourier Transform Infrared Spectroscopy (FTIR-1600, Shimadzu Co.). The samples were prepared by pressing the samples, which were ground with dried crystalline KBr.

Silica sample was immediately placed in a sealed AFM cell. The AFM (Digital Instrument, Nanoscope II) in the repulsive force range, with a tip load of ca. 5nN. Type NP cantilevers (Digital Instruments) were employed, which have Si3N₄ tips and a force constant equal to 0.38 kN/m. The recorded images are presented with or without filtering, which employed two-dimensional fast Fourier transform (FFT) and is noted in the captions. AFM pictures were taken by Digital Instriments Nanoscope II provided by Engineering Faculty of Yamanashi University, Japan.



CHAPTER 7

RESULTS AND DISCUSSION

The preparation of inorganic membranes by using sol-gel techniques was investigated in this work. The effects of water/alkoxide ratios, acid/alkoxide ratios on the properties of the unsupported membranes were examined.

The natures of the alumina sols are summarized in Table 7.1. The sol with lowest HNO_3 content (AlH0) remained unpeptized with a dense cake formation at the bottom of the bottle. The formation of a stable sol was not possible under these conditions. The sol with the highest H^+/Al^{+3} , Al5 and Al6 remained blurry.

Kod	H ⁺ /Al ³⁺	H ₂ O/Alkoxide	Appearance	
AlHO	0.1	200	Unpeptized	
AlH1	0.2	200	Clear sol	
AlH2	0.3	200	Clear sol	
AlH3	0.4	200	clear sol	
AlH4	0.5	200	Clear sol	
AlH5	0.6	200	Blurry	
Al1	0.2	200	Clear sol	
Al2	0.2	180	Clear sol	
Al3	0.2	160	Clear sol	
Al4	0.2	140	Clear sol	
Al5	0.2	120	Blurry	
Al6	0.2	100	Blurry	

Table 7.1. The nature of the Alumina Sols.

The peptization of the precipitated Alumina cake involves the stabilization of sol particles by loading the surfaces of the particles with H⁺ ions. Apparently in these sols some bigger particles remained and stabilized as agglomerates of crystallites. The high temperature aging process may involve dissolution- reprecipitation processes along with the formation of boehmite. A small fraction of these agglomerates may retain their structure and cause the formation of slightly blurry sols.

All the alumina sols were stable for about two years when stored at room temperature. The silica sols were all clear. They geled at room temperature during summer time. They were prepared again and stored in a refrigerator. These sols also gelled (about 10-17 wt % SiO₂) content) unless diluted significantly with ethanol.

Samples of these sols were further placed in polymeric petri-dishes and air dried for one day. These air-dried unsupported membranes were the inform of coherent thin films for the alumina sols but small thin pieces of glass in the air-dried silica membranes. These unsupported membranes were further heat treated at 400 °C (silica) and 600 °C (alumina) for 3 hours.

Kod	TEOS	Water	HNO ₃	Ethanol	Appearance
SiA	1	3	0.085	3.8	Clear Sol
SiB	1	4	0.085	3.8	Clear Sol
SiC	1	5	0.085	3.8	Clear Sol
SiD	1 all the	6	0.085	3.8	Clear Sol
SiE	1	6.4	0.085	3.8	Clear Sol
SiF	1 ples and	7	0.085	3.8	Clear Sol
SiG	1	8	0.085	3.8	Clear Sol
SiH	1	9	0.085	3.8	Clear Sol
SiJ	1	10	0.085	3.8	Clear Sol
SiL	1	15	0.085	3.8	Clear Sol
SiH1	1	6.4	0.01	3.8	Clear Sol
SiH2	1	6.4	0.05	3.8	Clear Sol
SiH3	1	6.4	0.085	3.8	Clear Sol
SiH4	1	6.4	0.1	3.8	Clear Sol

Table. 7.2. The nature of Silica Sols.

The size and morphology of the boehmite particles in the alumina sols primarily depend on the pH of these sols. The presences of fibrillar, plattey, granular and spherical particles of various sizes in the pH 3-5 range were reported previously (32,45). Fibrillar particles with aspect ratios (L, D) as high 50 were reported at a pH of 4.88 (32). The presence of relatively large plates along with plots of about 25 nm size were reported in another work (45).

Spherical particles of about 10nm were reported at a pH of 4.24 (32). The hydrolysis of Al^{+3} ions in solution is rather complex and a series of species can form depending on pH. The presence of the so-called 13,32 species $Al_{13}O_4$ ((OH)₂₄)⁺⁷ was reported earlier. This species was also reported to be the dominant species in the approximate pH range of 3.5-4.5 (82). The presence of such a species is probable in the precipitation of the sol particles of this work. The relative ratio of this particular species to the other polynuclear species is certainly a function of the sol preparation-dissolution-precipitation media.

The results of the thermal analysis of some of the unsupported alumina membranes are given in Figures 7.1-7.6 The following phase changes were reported to happen when Boehmite is heated to 1150-1200 °C (74).

AlO (OH) $\rightarrow \gamma$ -Al₂O₃ $\rightarrow \delta$ - Al₂O₃ $\rightarrow \alpha$ - Al₂O₃ 400°C 900 °C 1150 °C

Almost all the weight loss occurred at temperatures lower than 500-525 °C and the weight stabilized at a constant value up to 1000 °C. This behaviour is common in all alumina samples and was the main reason for the selection of 600 °C as the calcination temperature of the unsupported membranes. These membranes are mainly γ -Al₂O₃ after this heat treatment.

The amount of γ -Al₂O₃ formed was determined in the 62-43 % for AlH1-AlH4 and 60-62 % of the initial air-dried unsupported membrane weight. Their presences of four different weight loss stages are especially apparent in the AlH3 and AlH4 weight loss curves.

In the first stages (RT $\rightarrow \sim 80^{\circ}$ C) physical water and alcohol present in the pores of the membrane is leaving the material. The weight percent loss this stage is relatively constant in all alumina membranes and accounts to about 8-10% weight loss. The second stage (80 to about 270°C) may be due to the removal of chemically adsorbed – bound water- organics form the surface or interior of the alumina membrane and accounts to approximately 10-12 % weight loss. The removal of the present NO⁻³ groups from the membrane was thought to occur in the approximate range of 340-380 °C. The amount of this weight loss is maximum for sample AlH4 is evident from the stage of the curve given in Figure 7.32. The final stage where boehmite transforms to γ -Al₂O₃ (380-500 °C) the weight loss is about 7-11%.

The TGA curves of silica unsupported samples are presented in Figures 7.7-7.10. The 1000°C weight percentages of the samples are in the 76-82% range. In the first stage of weight loss in all samples up to 120°C, physical water is being removed from the membranes. The weight loss in this stage was in the 12-18% range. The weight loss percentages of SiE, SiA and SiL were 13%, 16% and 18% respectively. This shows agreement with the single point pore volumes of these three samples; 0.1717 cc/g, 0.2 cc7g and 0.253 cc/g temperature range at about 120-250°C. In the final stage of weight loss a gradual weight loss was observed up to about 1000°C. This accounts to about 4-6% total weight loss and was attributed to the removal of adsorbed-chemically bound water and residual organics.



Figure 7.29. TGA curve for AlH1/Al1.



Figure 7.30. TGA curve for AlH2.



Figure 7.3. TGA curve for AlH3.



Figure 7.4. TGA curve for AlH4.



Figure 7.5. TGA curve for Al3.



Figure 7.6. TGA curve for Al4.



Figure 7.7. TGA curve for SiA.



Figure 7.8. TGA curve for SiL.



Figure 7.8. TGA curve for SiE/SiH3.





Figure 7.9. TGA curve for SiH1



Figure 7.10. TGA curve for SiH2

The FT IR spectra of uncalcined and calcined alumina unsupported membranes are given n Figures 7.11-7.16. Infrared transmission spectra for uncalcined alumina samples indicate isopropyl alcohol (OH) and NH_3^+ peaks which are coincide at 1380 cm⁻¹. This peak disappeared in the calcined alumina samples. All defined peaks at 1070, 740, 600, 475 cm⁻¹ were found in spectra for uncalcined samples. These peaks were reported tobe due to the Al-Oh (boehmite) bending vibration (77). For calcined sample the region between 1000-400 cm⁻¹ can be defined as Al-O bending.

The spectra of all alumina samples indicate the presence of water at 1650 cm⁻¹ and broad peak at 3500 cm⁻¹ for both calcined and uncalcined samples. Samples were not kept in a desiccator to prevent moisture adsorption so this is the result of water peaks at FT IR spectra (77). The peaks at 2325 cm⁻¹ were reported as CO₂ peaks (75).

The FT IR spectra of uncalcined and calcined silica unsupported membranes are given in Figures 7.17-7.20. The band at 3450 cm⁻¹ is attributed to the stretching and deformation modes of hydroxyl groups and molecular water (75). And also there is another water peak at 1650 cm⁻¹ for both calcined and uncalcined samples (75,77). The peak at 1050 cm⁻¹ is attributed to transverse Si-O-Si asymmetric stretching modes. The bend at 800 cm⁻¹ corresponding to symmetric Si-O-Si stretches (75). Another well-known peak for silica samples at 460 cm⁻¹ is attributed to vibrational modes of tetrahedral SiO₄ (78,79). Uncalcined silica unsupported membrane show a bond at 1380 cm⁻¹ associated with the NH⁺³ and alcohol, which coincide each other.



Figure 7.11.FTIR spectrum for uncalcined and calcined unsupported membranes AlH1/Al1.



Figure 7.12.FTIR spectrum for uncalcined and calcined unsupported membranes AlH2.



Figure 7.13.FTIR spectrum for uncalcined and calcined unsupported membranes AlH3.



Figure 7.15.FTIR spectrum for uncalcined and calcined unsupported membranes Al3.






Figure 7.17.FTIR spectrum for uncalcined unsupported membranes SiL.









10.00

Figure 7.19.FTIR spectrum for uncalcined and calcined unsupported membranes SiH1.



Figure 7.20.FTIR spectrum for uncalcined and calcined unsupported membranes SiH2.

Adsorption- desorption isotherms for the alumina unsupported membranes are given in Figures 7.21 to 7.31. These isotherms are of Type IV isotherms typical of mesoporous and macroporous materials. The hysteresis loops resemble to H2 type loops commonly observed for materials with interconnected pore networks with different size and shapes (83). The N₂ adsorption- desorption isotherms for SiA and SiL are given in Figures 7.32 and 7.36. All the silica isotherms are of Type I typical of micropores materials.

These isotherms were used for the preparation of the cumulative pore volume and pore size distribution (dV/dD) versus pore diameter plots by using BJH desorption data and are presented in Figures 7.37 to 7.46 for unsupported alumina membranes. Similar pore volume and pore size distribution plots for another series of mesaporous Titania materials are presented in Figures 7.47 to 7-50 for comparison purposes. The pore size distribution plots for the microporous silica membranes prepared by using adsorption data by Horvath-Kawazoe method are presented in Figures 7.52 to 7.56. The surface area, pore size, pore volume, pore %, monolayer volume and volume adsorbed data is further tabulated in Table 7.3, 7.4 and 7.5. Similar information is given in Table 7.6 and 7.7 for the silica samples.

The total volume adsorbed varies in the range of 110-145 cm³/g STP for the alumina membranes. The monolayer volume, Vm in the 43-61.4 cm³/g STP. The desorption curves steeply go down at about P/Po \approx 0.5 and the adsorption – desorption curves coincide at and below P/Po \approx 0.4. Exceptions to this trend were in the isotherms of AlH2 and AlH3 where P/Po values for desorption started at 0.55 and 0.6 respectively. The desorption pore size distribution of AlH3 (Figure 7.39) represent a wider pore size distribution and a large fraction of pores about 45 A. The BET surface area of the AlH3 sample was determined to be the lowest in the AlH series as shown in Figure 7.57. The BET surface area of the Al series gave a maximum at a water/alkoxide ratio of 140 as shown in Figure 7.58. These differences in surface areas and pore size distributions may be attributed to the differences in the particle size- oligomeric species concentrations and sizes. The pH and solution chemistry of the sol of AlH3 may favour the formation of a higher percentage polymeric species in solution.



Figure 7.21. Nitrogen adsorption and desorption isotherm for AlH1.







Figure 72.3. Nitrogen adsorption and desorption isotherm for AlH3.



Figure 7.24. Nitrogen adsorption and desorption isotherm for AlH4.







Figure 7.25. Nitrogen adsorption and desorption isotherm for AlH5.



Frence 7.27. Nitrogen adsorption and desorption isotherm for Al2.



Figure 7.26. Nitrogen adsorption and desorption isotherm for Al1.



Figure 7.27. Nitrogen adsorption and desorption isotherm for Al2.



Figure 7.28. Nitrogen adsorption and desorption isotherm for Al3.



Figure 7.29. Nitrogen adsorption and desorption isotherm for Al4.



Figure 7.30. Nitrogen adsorption and desorption isotherm for A15.



Figure 7.31. Nitrogen adsorption and desorption isotherm for Al6.



Figure 7.32. Nitrogen adsorption and desorption isotherm for SiA



Figure 7.33. Nitrogen adsorption and desorption isotherm for SiL.



Figure 7.34. Nitrogen adsorption and desorption isotherm for SiE.



Figure 7.36. Argon adsorption and desorption isotherm for SiL.



Figure 7.35. Argon adsorption and desorption isotherm for SiA.



Figure 7.36. Argon adsorption and desorption isotherm for SiL.

KOD	Single Point Surface Area at P/Po (m ² /g)	BET Surface Area (m ² /g)	Langmiur Surface Area (m ² /g)	Average Pore Diameter by BET	Pore Diameter by BJH Adsorption	Pore Diameter by BJH Desorption
AlH1	209.0484	217.8937	304.0769	37.8879	36.8722	32.2811
AlH2	249.6222	258.5729	370.1898	38.2059	37.2071	33.0380
AlH3	179.8790	187.1635	267.7119	36.4571	39.6262	32.1885
AlH4	247.4525	257.6088	371.2479	32.4522	32.3900	31.9879
AlH5	256.3759	267.3316	385.5778	33.5783	31.8522	30.1390
Al1	209.0484	217.8937	304.0769	37.8879	36.8722	32.2811
Al2	205.0491	211.0327	293.9841	36.6092	32.4441	31.4461
Al3	208.6772	215.0085	292.5642	33.6113	34.7031	31.5056
Al4	239.6173	248.4296	343.4321	297920	33.0079	30.6035
Al5	217.1734	223.7733	359.3142	37.4875	36.5154	32.2542
Al6	189.6967	194.2016	288.3713	37.1871	31.6915	32.6309

Table 7.3. Surface Areas and Pore Diameters of Alumina Unsupported Membranes

A similar trend can be observed in the Titania gel pore size distributions. As the solids content of the sols increases from TC1 to TC8 the pore size also increases. This can be clearly observed for the pore size distribution of the TC8 sol (Figure 7.51). As the solids content increases in the Titania sol the size of the polymeric species most likely increases forming bigger particles upon calcination. The adsorption isotherm for AlH3 stabilized at a higher P/Po level (≈ 0.9), which also effects the adsorption pore, pore size distribution giving a certain amount of pores above 100 A in the BJH adsorption pore size distribution.

The BJH desorption pore diameter in the lowest for AlH5 as given in Table 7.3. The adsorption pore size was the lowest again for AlH5 and the highest for AlH3. The pure contents of the alumina membranes varied in the 35-44 % of total volume as calculated by using single point cumulative pore volume. For a majority of the membranes the calcined alumina samples were about 60% dense.

	ργ	Single Point	BJH Ads.	BJH Des.	Total	Solid	Pore
	(g/cm ³)	Cumulative Pore	Pore	Pore	Solid	%	%
		Volume(cm ³ /g)	Volume	Volume	Content		
AlH1	3.2	0.205925	0.196792	0.222127	0.5184	60.28	39.72
AlH2	3.2	0.241696	0.204728	0.218639	0.5542	56.39	43.61
AlH3	3.2	0.171162	0.18949	0.183437	0.4837	64.60	35.40
AlH4	3.2	0.211778	0.189647	0.202362	0.5243	59.60	40.40
AlH5	3.2	0.208984	0.159870	0.196682	0.5215	59.92	40.08
All ·	3.2	0.205925	0.196792	0.222127	0.5184	60.28	39.72
Al2	3.2	·0.191036	0.156968	0.207338	0.4695	62.07	37.93
A13	3.2	0.180233	0.201609	0.209230	0.5141	63.43	36.57
Al4	3.2	0.183926	0.163893	0.169861	0.4764	62.95	37.05
Al5	3.2	0.209717	0.227998	0.225547	0.5405	59.84	40.16
Al6	3.2	0.16867	0.130615	0.197106	0.4431	64.91	35.09

Table 7.4. Pore Contents and Densities of Alumina Unsupported Membares

Table 7.5. BET Surface Area, Monolayer and Total Volume of Nitrogen Adsorption forAlumina Samples

Samples	BET Surface Area	Monolayer Volume	Volume Adsorbed	$\Delta V = Va-Vm$
	(m²/g)	Vm (cm ³ /g STP)	Va (cm ³ /g STP)	
AlH1/ Al1	217.8937	49.8579	130	81.5
AlH2	256.5827	58.9412	145	86.5
AlH3	187.1635	187.1635	110	67
AlH4	257.6088	59.1769	136	77
AlH5	267.3316	61.4104	135	74
Al2	211.0327	48.4776	123	74
A13	215.0085	49.3900	116	67
Al4	248.4296	57.0683	118	61
A15	223.7733	51.4043	135	84
Al6	194.9547	44.7840	110	65



























Figure 7.42.BJH cumulative pore volume (a) and pore size distribution (b) plots for Al2.

Pore Diameter (A°)













































Pore Diameter (A°)











Figure 7.52. Horvath-Kawazoe plot from nitrogen adsorption for SiA.



Figure 7.53. Horvath-Kawazoe plot from nitrogen adsorption for SiL.









Figure 7.55. Horvath-Kawazoe plot from argon adsorption for SiA.







Figure 7.57. BET surface area versus H^+/AI^{+3} ratios for AlH1 to AlH5.



Figure 7.58. BET surface Area versus Water/Alkoxide ratios for Al1 to Al6.

volume adsorbed approximate' Figures 7.35-7.36 stab values than the Nitroge sol was 570 m²/g as (Water:6.) and increases samples were 4.17, 4.6 ai (Table 7.6).

SiL sample has lowest den 7.7). The single point cum micropore volume of all san

The adsorption- desorption isotherms for the BET -> 4 m2 dia

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sample was about 0.1 cc/g. T ... mcrease in the Langmiur surface area can be due to the fact that very fine pores in the other two samples were not polymeric species in the acidcatalyzed sol with the SiL composition may be bigger giving rise to a high single point cumulative pore volume.

Table 7.	6. Surface	Areas,	Micropore	Volume	and Pore	Diameter	for Silica	Unsuppo	orted
	Membra	anes							

	Single Point	BET	Langmiur	Micropore	Median Pore	
	Surface Area at	Surface Area	Surface Area	Volume	Diameter	
	P/Po (m²/g)	(m²/g)	(m²/g)		(HK) A°	
SiE	413.1823	404.6381	476.7346	0.144612	4.60	
SiA	445.3966	432.0035	570.8116	0.164094	4.17	
SiL	551.3103	543.4116	720.9741	0.155210	4.46	
SiA-A	345.1564	352.9673	435.9306	0.083715	6.22	
SiL-A	393.6379	400.5466	535.4251	0.053477	7.01	
	ργ	Single Point	Micropore	Total	Solid	Pore
-------	----------------------	----------------------	-----------	---------	-------	-------
	(g/cm ³)	Cumulative	Volume	Solid	%	%
		Pore Volume	2.653	Content		
		(cm ³ /g)	5.00			
SiA	2.2	0.200014	0.164094	0.65464	70.41	29.59
SiE	2.2	0.171714	0.144612	0.62621	72.58	27.42
SiL	2.2	0.252885	0.15521	0.70738	64.25	35.75
SiA-A	2.2	0.145951	0.083715	0.60050	75.69	24.31
SiL-A	2.2	0.170379	4,360	0.62490	72.73	27.33

Table 7.7. Pore Contents and Densities of Silica Unsupported Membares

The pore sizes of these silica membranes were determined by Horvath-Kawazoe (HK) techniques and different pore models using the ASAP 2010 software in the P/Po range of 0-0.1. These are further tabulated in Table 7.8. The pore sizes determined by all methods for all samples fall in the 4-10 A^o range. The Argon adsorption pore sizes are generally higher whereas Nitrogen- adsorption pore sizes fall in the 4.1-5.7 A^o range except the cylinder (Saito/Foley) pore geometry. He reasons behind the differences in these pore sizes are still under investigation. The main result to emphasize would be the presence of 4-5 A^o pores in these membranes which are good candidates of molecular sieves. These pore sizes may also be size range by the careful design of the preparation conditions.

Table 7.8. Horvath-Kowazoe techniques at Different Pore Models

Sample	HK slit	HK cylinder (Saito/Foley)	HK sphere	HK sphere (Chang-Yang)
SiA	5.0	8.7	4.2	4.1
SiE	5.7	4.8	5.2	5.0
SiL	5.3	9.1	4.6	4.5
SiA-A	7.4	6.0	7.7	7.2
SiL-A	8.6	7.4	9.6	9.1

Sample	Surface Area (m ² /g)	r (nm)	D (A°)
AlH1	217.8937	4.3026	86
AlH2	256.5827	3.6538	73
AlH3	187.1635	5.009	100
AlH4	257.6088	3.6392	73
AlH5	267.3316	3.5069	70
Al1	217.8937	4.3026	86
A12	211.0327	4.4424	89
Al3	215.0085	4.3603	87
Al4	248.4296	3.7737	76
A15	223.7733	4.1895	84
Al6	194.9547	4.8088	96
TC1	105,4119	8.8937	178
TC2	98.727	9.4959	190
TC5	103.4346	9.0637	181
TC6	82.519	1.1361	227
TC8	100.9593	9.2859	186
SiA	570.8116	1.6424	33
SiE	476.7346	1.9665	39
SiL	720.9741	1.3003	26
SiA-A	435.9306	2.1506	43
SiL-A	535.4251	1.7509	35

Table 7.9. Particle Sizes for Alumina, Titania and Silica Unsupported Membranes

(In Table 7.9 BET Surface area were used for Alumina and Titania sample, Langmiur Surface Area were used for Silica samples)

The BET surface areas of porous materials is commonly used for a simple estimation of the median particle size. The surface area is simply equated to 3/(p.r) where r is the radius of the monosize spherical particles forming the porous material and p is the density of the material. The particle sizes of the unsupported alumina and silica samples investigated in this work along with titania samples characterized in an earlier work (84) is tabulated in Table 7.9. The particle sizes of the alumina samples vary in the 70-100 A° (7-10 nm) range. The titania particles were determined to be significantly bigger (more than two times) with sizes in the 178-227 A° (18-23 nm). These sizes were in agreement with the previously reported particle sizes. The silica particle sizes varied in between 26-43 A° (2.6-4.3 nm) by using the Langmiur surface areas.

In isotherms exhibiting hysteresis (as was observed in all the mesoporous alumina and titania membranes of this work), the adsorption branch is thought to be controlled by the cavities or pores in the material whereas the desorption branch is controlled by the throat sizes (sizes of the entrances to the cavities aor pores). The hysteresis results from the differences in the sizes of the throats and the cavities. However the adsorption-desorption isotherms of the silica membranes didn't show hysteresis.

The use of BJH desorption isotherm for the determination of the actually pore size distributions may be in error. These pore size distributions may actually be called as "opening or throat" size distributions in these mesoporous materials. The BJH adsorption isotherm based pore size distributions represent the actual cavity (pore) distributions in materials formed by the packing of spherical or equiaxed particles. The form of these hysteresis loop may also present information about the interconnectetivity of the pore network. It was further discussed that depending on the nature of this pore network some pores may even be left unfilled even at P/Po ≈ 1 giving rise to a lower total pore volume from the N₂ adsorption isotherms(83). The existence of this phenomena must be checked by pore volume-density determination by using other methods.

The overall pore volume, cavity size and throat size of a material formed by the packing of monosize spheres depend on the size of the spheres and the co-ordination number. These important parameters were tabulated in Table 7.10 for monosize sphere packing.

Packing Type	Co-ordination number	Porosity %	Radius of sphere inscribed in cavities	Radius of sphere inscribed in throats
Rhombohedral (Cubic Hexagonal)	12	25.95	0.2247R 0.4142R	0.1547R
Tetragonal	10	30.98	0.2910R-	0.1547R 0.2649R
Body-centered Cubical	8	31.98	0.2910R	0.2247R
Orthorhombic (Primitive hexagonal)	8	39.54	0.5275R	0.1547R 0.4142R
Cubic	6	47.64	0.732R	0.4142R

Table 7.10. Important characteristics of some monosize sphere packings (85).

The densest sphere packing in theoretically achived with a co-ordination number 12 and pore content of about 26% of the total volume. Random packing of spheres usually result in about 40% porosity and a co-ordination number close to 8. There are tetrahedral and octohedral cavities in the densest packed structures. These are throats with sizes in the 0.1547 to 0.4142 of the sphere size (D) in sphere packing with co-ordination (CN) number in the 8-12 range. The sizes of the cavities in the same range is 0.2247-0.5275 D.

The particles in the alumina membranes had sizes in the 70-100 A° range with porosities close to about 40% (35-44 % of total volume). The sizes of the throats with CN=8 from the Table 7.10 for this particle range should be in the 29-41 A° range for big openings and 11-15 A° for small openings.

The BJH desorption pore size range for these samples were determined as about 30-33 A° (Table 7.3). This falls in the 29-41 A° theoretical throat size range. The corresponding theoretical cavity size range is 37-53 A° . The determined BJH adsorption pore size range was 32-40 A° . The agreement in the theoretical-experimentally determined throat size ranges seems to be reasonably good. The cavity (pore) size agreement looks worse. Similar correlations between the theoretical throat-pore sizes (assuming BET particle sizes as monosize sphere sizes) and the experimentally determined throat pore size ranges represented reasonable agreement. Silica unsupported membrane sample (SiE) after heat treatment was examined by atomic force microscopy (AFM). Silica sample was about 1mm thick and had a relatively hard glassy surface. AFM characterizations of the unsupported alumina membrane samples were not possible because of the fragile nature of the relatively soft thin membrane films.

Three dimensional AFM images of SiE unsupported membrane surface are shown in Figures 7.59 to 7.62. It is relatively easy to see smooth surface of the sample at a high z range (z=4nm). The image given in Figure 7.62 has a similar surface structure which was taken five hours after the Figure 7.59, 60, 61 images.



Figure 7.59. Atomic force microscopy (AFM) image for SiE sample at z=4nm.

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Figure 7.60. Atomic Force microscopy (AFM) image for SiE sample at z=4nm.

It was not possible to obtain pore size information from these images. These images especially images in Figure 7.61 and 7.62, can give a valuable information about the scale of the surface roughness.

As can be seen clearly in Figure 7.61, the top layer shows a surface roughness with a maxima of around 2.5-5 A° . Five hours after the images in Figure 7.61 another an image (Figure 7.62) was obtained which has a similar uniform roughness in the 2.5 – 5 A° range.

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Figure 7.61. Atamic force microscopy (AFM) images for SiE sample at z=2.5nm.



Figure 7.62. Atomic force microscopy (AFM) images for SiE sample at z=1.3nm.

CONCLUSIONS AND RECOMMENDATIONS

The results of this work have shown that it is possible to prepare membranes with relatively sharp-fine pore size distribution by using sol-gel techniques. The preparation and further processing steps have significant effects on the pore structure of these membranes.

Unsupported γ - Alumina membranes prepared from boehmite sols all displayed Type IV Nitrogen adsorption-desorption isotherms typical of mesoporous materials. The adsorption pore sizes of these membranes were in the 30-33 A^o range. The desorption pore size distributions were uniform with almost no pores bigger than 40-45 A^o. An exception to this was the behaviour of the AlH2-AlH3 samples where H⁺/Al⁺³ ratios were 0.3 to 0.4. The BET surface area of the AlH3 sample was the lowest at 187 m²/g and had a wider desorption pore size distribution. The adsorption pore sizes were generally bigger and had a wider distribution. The BET particle sizes of these samples were determined to be in the 70-100 A^o range.

The TGA anlaysis have shown that there are primarily four stages in the weight loss curves of the unsupported Al_2O_3 membranes. Theses were concluded to be due to the removal of water from the pores, the removal of adsorbed- chemically bound water, the NO₃ removal and the decomposition of the boehmite to γ - Al_2O_3 at about 425 °C. The TGA analysis of the silica unsupported membranes have shown a two-stage thermal behaviour, the removal of physical water from the pores and adsorbed- chemically bound water.

All the silica samples displayed Type I isotherms characteristic of microporous materials. The Nitrogen adsorption isotherm based on Horvath-Kawazoe, pore sizes were determined to be in the 4.1- 5 A^o range. The pore size showed a dependence on the water content of the originally clear silica sols. The reasons for the differences in the pore sizes should be further investigated. The AFM images of one of these membranes did show the presence of surface roughness in the 2.5-5 A^o range.

The comparison of adsorption and desorption pore sizes with throat-cavity sizes of the theoretical monosize sphere packings with different coordination numbers (different pore content) have shown reasonable agreements. These aggreements support the fact that nearly spherical particles do exist in these membranes. SEM analysis of the particle size and morphology would represent further support to the comparison of these theroticalexperimental pore sizes.

Argon adsorption-desorption isotherms on the mesoporous alumina-titania membranes and the SiH series would yield valuable information on the effect of sol preparation on the membrane pore structure. Independent pore volume determination techniques like water displacement, adsorption or mercury porosimetry can give valuable information on the pore interconnectivity - network in these mesoporous materials.

The final recommendation of this work would be the use of these membrane materials in gas permeation. This also can give information on the pore structure of chemically identical materials. e

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