SYNTHESIS AND CHARACTERIZATION OF SUPERHYDROPHOBIC ALUMINA MEMBRANE VIA CHEMICAL AND MORPHOLOGICAL MODIFICATION

By

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LIST OF SYMBOLS

θ	Angle of water (^{o})
^{o}C	Temperature (Celsius)
%	Percentage
% w/w	Percentage by mass/mass
h	Time in hour
L	Volume of liquid in Litter
m	Length in metre
min	Time in minutes
ml	Volume in millilitre
Ra	Average roughness
s	Time in second
w%	Weight percent

LIST OF ABBREVIATIONS

AFM	Atomic Force Microscope
Al_2O_3	Alumina oxide
ASB	Aluminum-tri-sec-butoxide
CA_w	Water contact angle
CO_2	Carbon Dioxide
EDX	Energy-dispersive X-ray spectroscopy
F0	Membrane support
F0.1	Direct grated membrane with 0.1 ml HFDS:50 ml ethanol
F0.5	Direct grated membrane 0.5 ml HFDS:50 ml ethanol
F1.0	Direct grated membrane 1.0 ml HFDS:50 ml ethanol
F2.5	Direct grated membrane 2.5 ml HFDS:50 ml ethanol
FAS	Fluoroalkysilane
HFDS	**(**Heptadecafluoro-1,1,2,2-tetra hydrodecyl) triethoxysilane
LEP_w	Liquid entry pressure of water
OH	Hydroxyl group
PES	Polyethersulfone
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
SC	Grafted membrane with calcined sol coated layer at 450 ^oC
SEM	Scanning electron microscope
SS	Grafted membrane with steam sol coated layer
SSS	Grafted membrane fabricated via dip coated in sol-gel with various time then treated with steam for 1 min and hot water at 100 ^oC
SSV	Grafted membrane fabricated via dip coated in sol-gel for 1 min then treated with various steam duratios and hot water at 100 ^oC
SST	Grafted membrane fabricated via dip coated in sol-gel for 1 min then treated with steam for 1 min and treated with different water temperatures
UPE	Unsaturated polyester

SINTESIS DAN PERINCIAN MEMBRAN ALUMINA SUPERHIDROFOBIK MELALUI KAEDAH KIMIA DAN PENGUBAHSUAIAN MORFOLOGI

ABSTRAK

Hidrofobik ialah sifat "hindar air" pada sesuatu permukaan. Walaupun membran seramik mempunyai kekuatan mekanikal yang tinggi, rintangan kimia yang cemerlang dan kestabilan haba yang hebat, ciri-ciri semula jadi hidrofilik membran seramik menghadkan penggunaannya. Pengubahsuaian membran menggunakan kaedah cantuman silan telah dilaporkan secara meluas kerana pengendalian yang mudah, tetapi pertumbuhan struktur hidrofobik memperkenalkan rintangan tambahan dalam pemindahan jisim. Tujuan utama dalam kajian ini, adalah untuk mensintesis membran superhidrofobik dengan rintangan membran yang minimum. Dalam kajian ini, kesan kepekatan (heptadecafluoro-1,1,2,2-tetra hydrodecyl) triethoxysilane (HFDS) pada rintangan pemindahan jisim membran alumina superhidropobik dikaji. Selain cantuman langsung, cantuman HFDS turut dilakukan pada filem alumina nipis yang disediakan melalui kaedah sol-gel dengan pengkalsinan atau kaedah stim untuk mengurangkan liang tersumbat. Pada permulaannya, sokongan alumina dicantum secara langsung dengan perbezaan nisbah isipadu HFDS terhadap etanol (0,1-2,5 ml HFDS:50 ml etanol). Cantuman langsung HFDS pada membran memberikan sudut sentuhan air statik dalam lingkungan 85.84 ^{o} (0.1ml HFDS) hingga 138.91 ^{o} (1.0 ml HFDS). Peningkatan kepekatan HFDS, menyebabkan liang membran tersumbat ekoran daripada penembusan rantaian HFDS. Jumlah rintangan membran meningkat daripada $4.05\text{x}10^{10}$ m^{-1} hingga $1.52\text{x}10^{12}$ m^{-1} selepas bercantum dengan 2.5 ml HFDS. Bagi menghasilkan membran superhidrofobik kaedah sol-gel telah digunakan untuk menghasilkan permukaan kasar sebelum cantuman silan. Selanjutnya, pengkalsinan lapisan alumina sol-gel pada suhu 450 °C dan cantuman silan dengan 1 ml HFDS meningkatkan sudut sentuhan air sehingga 148.9 °. Sudut sentuhan air sedikit tinggi dicatatkan iaitu 158.4 ° pada membran sol-gel selepas kaedah stim dan cantuman HFDS dengan nisbah 1 ml HFDS kepada 50 ml etanol. Kaedah sol-gel bukan sahaja meningkatkan kekasaran permukaan malah rintangan di dalam membran dapat dikurangkan berbanding cantuman langsung membran dengan kepekatan HFDS yang sama. Kaedah stim menggalakkan pembentukan kesan meteor pada bumi yang membentuk kawah, menjana permukaan dengan mikro dan nano kekasaran untuk mencapai sifat superhidrofobik. Kesan kaedah stim, membran sol-gel mempunyai rintangan membran yang lebih rendah dan mengurangkan liang tersumbat berbanding dengan membran sol-gel dikalsin pada suhu 450 °C. Tambahan itu, parameter yang berbeza dikaji dengan menggunakan kaedah stim seperti masa salut celup sol-gel, tempoh stim dan rendaman pada suhu air yang berbeza. Lapisan sol-gel yang terhasil kurang dari 7 saat salutan celup, dirawat dengan stim selama 1 min dan direndam di dalam air pada suhu 100 ^{o}C selama 10 minit disyorkan menghasilkan membran alumina superhidrofobik dengan rintangan membran yang minimum. Membran alumina superhidrofobik telah berjaya digunakan dalam pembersihan minyak tanah untuk penyingkiran air dalam emulsi air-minyak. Kira-kira 99 % daripada air yang dikeluarkan dari emulsi air-minyak dan penelapan fluks lebih daripada 100 ml/min diperhatikan sepanjang penapisan.

SYNTHESIS AND CHARACTERIZATION OF SUPERHYDROPHOBIC ALUMINA MEMBRANE VIA CHEMICAL AND MORPHOLOGICAL MODIFICATION

ABSTRACT

Hydrophobicity is commonly known to have “water repellent” feature on a surface. Although ceramic membranes possess superior mechanical strength, excellent chemical resistance and great thermal stability, the natural hydrophilic feature of ceramic membranes limits their applications. Membrane modification by silane grafting has been widely reported due to its ease of handling, but the growth of hydrophobic structure introduces additional resistance in mass transfer. The major aim of this study is to synthesis superhydrophobic membrane with minimum membrane resistance. The effects of (heptadecafluoro-1,1,2,2-tetra hydrodecyl) triethoxysilane (HFDS) concentration on mass transfer resistance of superhydrophobic alumina membrane is studied as well. Besides direct grafting on membrane, HFDS was grafted on the additional thin alumina films prepared by sol-gel method with calcinations or steam treatment in order to reduce pore blockage. Alumina supports were first directly grafted with different volume ratios HFDS in ethanol (0.1-2.5 ml of HFDS:50 ml of ethanol). The HFDS grafted membranes showed static water contact angle in the range of 85.84 ^{o} (0.1ml of HFDS) to 138.91 ^{o} (1.0 ml of HFDS). The increment of HFDS concentration, however, caused membrane pore blockage due to the penetration of HFDS chain. Total membrane resistance increased from $4.05x10^{10}$ m^{-1} to $1.52x10^{12}$ m^{-1} after grafting with 2.5 ml of HFDS. In order to produce superhydrophobic membrane, sol-gel method was used to create rough surface before silane grafting. Further calcination of the sol-gel alumina layer at 450 °C and silane grafting with 1 ml of HFDS improved the water contact angle up to 148.9 ^{o}. A slightly higher water contact angle of 158.4 ° was recorded for the sol-gel membrane after steam treatment and HFDS grafting with 1 ml of HFDS in 50 ml of ethanol. Sol-gel method not only enhanced surface roughness but also reduced membrane resistance in membrane compared to direct grafted membrane with the same grafting concentration. Steam treatment encouraged the formation of a surface with crater like due to meteor striking earth effect, generating surface with micro-roughness and nano-roughness to achieve superhydrophobicity. After steam treatment, sol-gel membrane has lower membrane resistance and pore reduction compared to the sol-gel membrane calcined at 450 °C. Thus, different parameters in steam treatment such as sol-gel dip coating time, steam duration and water temperature have been further studied. Sol-gel coating prepared under 7 s of dip coating, steam treated for 1 min and immersed in 100 ^{o}C of water for 10 minutes are recommended for synthesis of the superhydrophobic alumina membrane with minimum membrane resistance. The superhydrophobic alumina membrane was successfully applied in kerosene purification, for the removal of water-in-oil emulsion. About 99 % of the water was removed from the water-oil emulsion and a permeate flux more than 100 ml/min was observed throughout the filtration.

CHAPTER 1

INTRODUCTION

1.1 Superhydrophobic Membrane

Membranes with low surface energy, large liquid entry pressure, fast permeation of nonpolar molecules, excellent rejection of polar compound, great mechanical strength and outstanding chemical stability are recently required in advanced membrane separation. Membranes with superhydrophobic feature (water contact angle >150 ^{o}) are most desirable in membrane distillation, osmotic evaporation, membrane gas absorption and filtration. Hydrophobic membranes have been successfully applied in membrane distillation for desalination, with salt rejection reported to be higher than 90 % at a feed temperature more than 90 ^{o}C (Cerneaux *et al.*, 2009; Krajewski *et al.*, 2006; Larbot *et al.*, 2004; Khemakhem and Amar, 2011; Hendren *et al.*, 2009; Gazagnes *et al.*, 2007). Hydrophobic membrane with a water contact angle of 139 ^{o} has also been effectively used to concentrate fruit juices (Vargas-Garcia *et al.*, 2011). Besides that, hydrophobic ceramic membranes showed great permeate flux in the filtration of non-polar organic solvents (Gao *et al.*, 2011).

Table 1.1 shows some of commercial hydrophobic membranes available for pervaporation, membrane distillation, membrane gas absorption and other applications. Hydrophobic polymeric membranes are commonly used due to their low cost, ease of preparation and wide range of commercial availability (Pierre and Christian, 2008).

Table 1.1: Commercial hydrophobic polymeric membranes and the manufacturers.

Supplier	Product	Base material	Features
Pervatech (Casado *et al.*, 2005)	SiO_2 over alumina, Pervatech PVP	SiO_2/ Al_2O_3	Water flux a) Water- acetone at 40 ^{o}C: 0.44 kg m^{-2} h^{-1} at 70 ^{o}C: 2.72 kg m^{-2} h^{-1} b) Water- isopropanol at 40 ^{o}C: 2 kg m^{-2} h^{-1} at 40 ^{o}C: 3.2 kg m^{-2} h^{-1} Water concentration: >99.5 wt%
Pall Corporation (Corporation, 2011a; Corporation, 2011b; Corporation, 2011c; Corporation, 2011d)	B cell-specific tetraspanning (BTS) Hydrophobic Membrane	Polysulfone (PSf)	Pore size (µm): 0.1-0.2 Liquid entry pressure of water (LEP_w) LEP_w: >3.4 KPa
	Hydrophobic Acrylic Copolymer Membrane	Acrylic copolymer	Pore size (µm): 0.2-10 LEP_w: >3.4 KPa
	Hydrophobic Polyethersulfone (PES) Membrane	PES	Pore size (µm): 0.2-0.45 LEP_w:82.7-393 KPa
	Hydrophobic Polyvinylidene fluoride (PVDF) Membrane	PVDF	Pore size (µm): 0.2-0.45
Membrana (Membrana, 2011)	Accurel Polypropylene (PP) flat membranes	PP	Pore size (µm): 0.1-0.2 Transmembrane flow: >2.5 ml/(min cm^2 bar) with 2-isopropanol
	Hydrophobic Polytetrafluoroethylene (PTFE) Membrane	PTFE	LEP_w : 800000 KPa
Millipore (Millipore, 2011b, Millipore, 2011a)	Hydrophobic SureVent Unsaturated polyester (UPE) Membrane	UPE	Pore size (µm): 0.05-1.0 Airflow rate (slpm/cm^2): 1.1-13.9 at 69 KPa
	Hydrophobic SureVent PVDF Membrane	PVDF	Pore size (µm): 0.1-5.0 LEP_w : 14-503 KPa

(Continued)

Table 1.1: Commercial hydrophobic polymeric membranes and the manufacturers.

Supplier	Product	Base material	Features
Cobetter Filtration (Cobetter, 2010)	Hydrophobic PTFE membrane	PTFE	Pore size (μm): 0.02-10.0 LEP_w: >500 KPa
Whatman (Whatman, 2011)	Hydrophobic PTFE membranes	PTFE	Pore size (μm): 0.2, 0.5 and 1 Liquid flow rate (69 KPa vacuum): 61.4-445 with acetone
Membrane Solution (Solutions, 2011)	Hydrophobic PTFE Membrane	PTFE	LEP_w : 800000 KPa
Sulzer Chemtech (Luis *et al.*, 2013)	Pervap 2255-50	Mixed polymers	Selectivity of Butyl acetate to methanol: 16 to 1 (20 to 80 mol% methanol) Total Flux: 0.2 to 1.2 kg/m^2h at 20 to 80 mol% methanol

However, polymeric membranes are morphologically unstable in corrosive medium, high operating temperature and/or pressure. Membrane deformation, membrane swelling and plasticization impaired the membrane performance which leads to higher operating cost and maintenance expenditure (Brodard *et al.*, 2003). The plasticization is the non-equilibrium state of the glassy polymers (polystyrene, Polycarbonate, polymethyl methacrylate) during membrane gas separation process. Due to these reasons, ceramic membranes with superior mechanical strength, excellent chemical resistance and great thermal stability are of great interest. Unlike polymeric membranes, ceramic membranes naturally possess hydrophilic characteristic because their metal oxides can form hydroxyl (OH) groups; encouraging adsorption of water (Mansur *et al.*, 2008). Thus, ceramic membranes must be modified into superhydrophobic ceramic membranes for the mentioned applications.

On the other hand, hydrophobic ceramic membranes have not been commercialized to our best knowledge. It may be related to the high mass transfer resistance, leading to limited application of the hydrophobic ceramic membrane. As the result, the commercialization of hydrophobic ceramic membrane has not been initiated.

1.2 Problem Statement

Ceramic membranes are naturally hydrophilic, show low rejection of polar components and permeate flux of non-polar species. The transformation of hydrophilic ceramic membranes into superhydrophobic membranes is urgently needed. The preparation of hydrophobic ceramic membranes via silane grafting has been widely reported (Gazagnes *et al.*, 2007; Krajewski *et al.*, 2006; Krajewski *et al.*, 2004; Picard *et al.*, 2004; Larbot *et al.*, 2004). However, the needle-like structure from silane grafting (Lu *et al.*, 2009) usually introduces an additional resistance in mass transfer. Besides reducing surface energy using organosilane, creating rough surface via surface erosion and sol-gel method allows the enhancement of surface hydrophobicity. Surface erosion by corrosive chemical could result enhancement of surface roughness but the effectiveness to create roughness is unpredicted and difficult to be controlled (Lu *et al.*, 2009; Guo *et al.*, 2006). Besides that, erosion can be strongly localized causing internal microstructure changes (Burggraaf, 1996). Due to these limitations, sol-gel method was proposed as an alternative to create great roughness without using any corrosive solvent (Han *et al.*, 2012; Tadanaga *et al.*, 2003, Tadanaga *et al.*, 1997a, Fang *et al.*, 2009; Zhang et al., 2009).Sol-gel thin layer introduces nano- roughness on ceramic membranes. In addition, the sol-gel film could be further physically treated to improve surface roughness. In this work, steam treatment is proposed to enhance surface roughness.

Nevertheless, the lack of understanding of sol-gel coating with various post-treatment steps could lead into the growth of membrane resistance due to the penetration of sol-gel particle instead of silane. Nandi *et al.*, (2009) reported that increasing dip coating time not only reduces the pore size and porosity, but also creates great resistance in the membrane. Meanwhile, long term steam treatment would reduce the surface roughness and induce the formation of dense layer due to the great kinetic energy of steam molecule exerted on the surface (Yang *et al.*, 2001). Thus, there is a need to further understand the method proposed earlier and to compare the effects of sol-gel, steam treatment and water treatment in detailed.

1.3 Research Objectives

The research objectives in this work are listed as shown below

i) To synthesis superhydrophobic alumina membrane with minimum membrane resistance via silane grafting and sol-gel coating with post treatments for kerosene purification.

ii) To study the effects of post treatment of sol-gel, steam treatment and water treatment to morphology changes of superhydrophobic alumina membrane.

1.4 Scope of Study

This study focused on the synthesis of superhydrophobic alumina membrane. The first section involves different synthesis methods to prepare superhydrophobic alumina membrane for kerosene purification. Two methods were compared, namely

(i) direct grafting with varied organosilane concentrations and (ii) sol-gel coating with various post treatments followed by silane grafting. In this work, steam treatment was suggested as the additional post treatment of sol-gel layers. Membranes were characterized in order to select the most appropriate method to produce superhydrophobic alumina membrane with minimum resistance. Similar organosilane was used for both methods, either direct grafting or sol-gel coating followed by silane grafting.

Sol-gel layer with post treatment was proposed not only to improve surface roughness, but also to reduce membrane resistance. Further study on the sol-gel and post treatments in the second section allows the precise control of membrane characteristics. Parameters such as sol-gel dip coating duration, steam treatment duration and water temperature were studied in detail. Similar to the first section, membranes were characterized to study the effect of post treatment of sol-gel, steam treatment and water treatment to morphology behaviour of superhydrophobic alumina.

1.5 Organization of the Thesis

This thesis consists of five chapters, provides all the details and findings of the research. The fives chapters are introduction, literature review, research methodology, result and discussion and lastly conclusion and recommendations.

Chapter one briefly explains about the introduction of the superhydrophobic, general membrane applications, commercial hydrophobic membranes available in market, problem statement, research objectives, scope of study and thesis organization.

Chapter two reviews all the related literatures on superhydrophobic membranes and this chapter is divided into two sub-chapters. First sub-chapter explains different routes used by researchers to prepare superhydrophobic or hydrophobic ceramic membranes. Preparation method can be divided into two routes; (i) chemical modification and (ii) morphological and chemical modification. Whereas, the second sub-chapter more on the comparison and various applications of hydrophobic membranes.

Chapter three is about the methodology used to start up the experiment. This chapter is divided into four sub-chapters (3.1, 3.2, 3.3 and 3.4). The first two sub-chapters are the brief introduction on chapter three and the chemicals used. Third sub-chapter (3.3) explains in detail the membrane preparation procedures and separates into two sections. First section is about the membrane preparation in producing of hydrophobic membrane for the kerosene purification. While, second section is about the synthesis of hydrophobic alumina membrane: effects of sol-gel coating, steam treatment and water treatment. The sub-chapters 3.4 and 3.5 are about the membrane characterization and kerosene purification.

Chapter four is the important chapter to describe all the experimental results and discussion in order to achieve two research objectives. This chapter is divided into three sub-chapters (4.1, 4.2 and 4.3). First sub-chapter (4.1) is the general introduction in chapter four. Second sub-chapter (4.2) discusses our finding on the first research objective; to synthesis superhydrophobic alumina membrane with minimum membrane resistance via direct silane grafting and silane grafting on sol-gel coating with post treatments for kerosene purification. Third sub-chapter (4.3) explains in detail our finding on the second research objective; to understand the effects of sol-gel, steam treatment and water treatment on membrane morphology and resistance in the preparation of superhydrophobic membrane using sol-gel method.

Chapter five presents a summary on the finding throughout this research. This chapter concludes all the research findings in the research work with several recommendations to improve future work.

CHAPTER 2

LITERATURE REVIEW

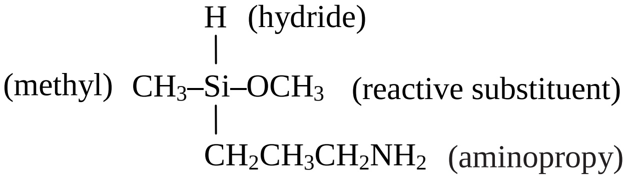
2.1 Preparation of superhydrophobic ceramic membrane

Ceramic membranes are naturally hydrophilic because their metal oxides possess hydroxyl (OH) groups; encouraging the adsorption of water (Mansur *et al.*, 2008). The conversion of a hydrophilic ceramic membrane into a hydrophobic ceramic membrane can be easily achieved by two routes; (a) chemical modification and (b) morphological and chemical modification.

2.1.1 Chemical modification using organosilane or lipid

Surface wettability is strongly affected by chemical groups on the surface which can be classified into either hydrophilic or hydrophobic groups. The common hydrophilic groups are –OH, $–COO^-$ and $Al_n(OH)_m$ while the general hydrophobic groups are $–CH_3$, $–CH_2–CH_2–$, and $–CF_3$. Surface tension of the typical substituent endgroups decreases in the following order: CH_2 (36 dyn/cm)> CH_3 (30 dyn/cm)> CF_2 (23 dyn/cm)> CF_3 (15 dyn/cm) (Dettre and Johnson Jr, 1966; Dettre and Johnson Jr, 1969; Bernett and Zisman, 1960). Chemical modification via grafting process allows the desired chemical groups to be introduced onto a substrate due to creation of hydrogen bond, ionic bond, Van der Waals forces or covalent bondings. Organosilane and lipid solution are generally used in the grafting process. Organosilane remains the most frequently used modifier as it requires a short treatment time with a simple procedure.

The name ‘silane’ refers to a molecule consisting of one Si atom connected with four functional groups, SiX_4. A silane that contains at least one carbon silicon bond (CH_3–Si–) structure is known as an organosilane (Xiameter, 2009a; Xiameter, 2009b; Yasutomo, 2008; Inc., 2006; Corning, 1995). Figure 2.1 shows an example of chemical structure of organosilane. The carbon-silicon bond which is very stable and non-polar gives rise to low surface energy, and hydrophobic effects. The silicon hydride (–Si–H) and the reactive substituent (–Si–OCH_3) structures are very reactive. These reactive structures react with the polar solvent to yield reactive silanol (–Si–OH) species by adding carbon-carbon double bonds to form new carbon-silicon-based materials. The methoxy group on the carbon compound determines effects of the silicon atom on chemistry of the organofunctional group. If the organic spacer group is a propylene linkage (e.g., –$CH_2CH_2CH_2$–), organic reactivity of the organofunctional silane will be similar to the organic analogs in the carbon chemistry (Xiameter, 2009b). Certain reactive silanes, particularly vinyl silanes (–Si–CH=CH_2) and silicon hydrides (–Si–H) are useful reactive groups in silicon chemistry, even though the reactive group is attached directly to the silicon atom.



$$\text{(methyl)}\ CH_3\text{–}\overset{\overset{\text{H (hydride)}}{|}}{\underset{\underset{CH_2CH_3CH_2NH_2\ \text{(aminopropy)}}{|}}{Si}}\text{–}OCH_3\ \text{(reactive substituent)}$$

Figure 2.1: An example molecule structure of organosilane compound.

2.1.1.1 Immersion in organosilane or lipid solution

Immersion of the ceramic membrane in organosilane or lipid solution is a simple procedure which requires a short time to produce hydrophobic ceramic membrane. In the organosilane grafting, the ceramic membrane is immersed directly into the reactive organosilane solution and then rinsed with the solvent to remove any excess organosilane. The reactive organosilane solution with active silanol is prepared by hydrolyzing organosilane in solvent like water (D. Schondelmaier, 2002, Sugimura, 2000), hexane (Lu *et al.*, 2009) and alcohol (Fang, 2009; Xiaoxue Zhanga, 2008). Figure 2.2 shows hydrolysis of the organosilane in solvent to form active silanol species. The reactive substituent, X like halogen and alcohoxy groups in the organosilane molecules are converted to OH groups (Inc., 2006, Corning, 1995).

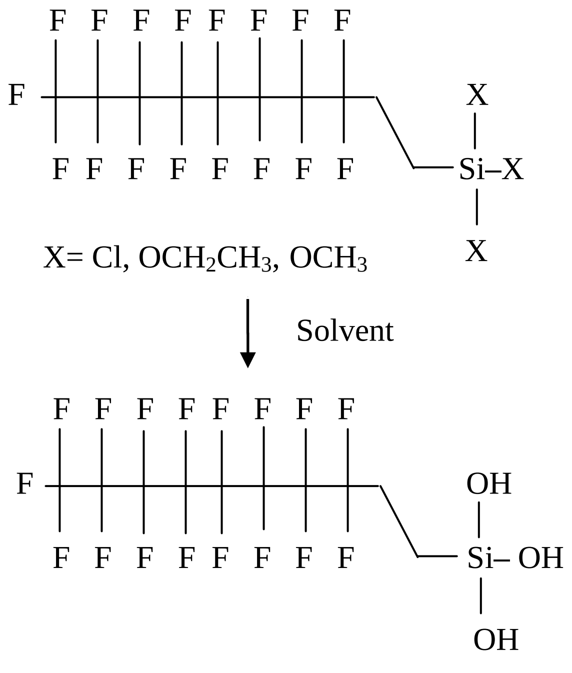
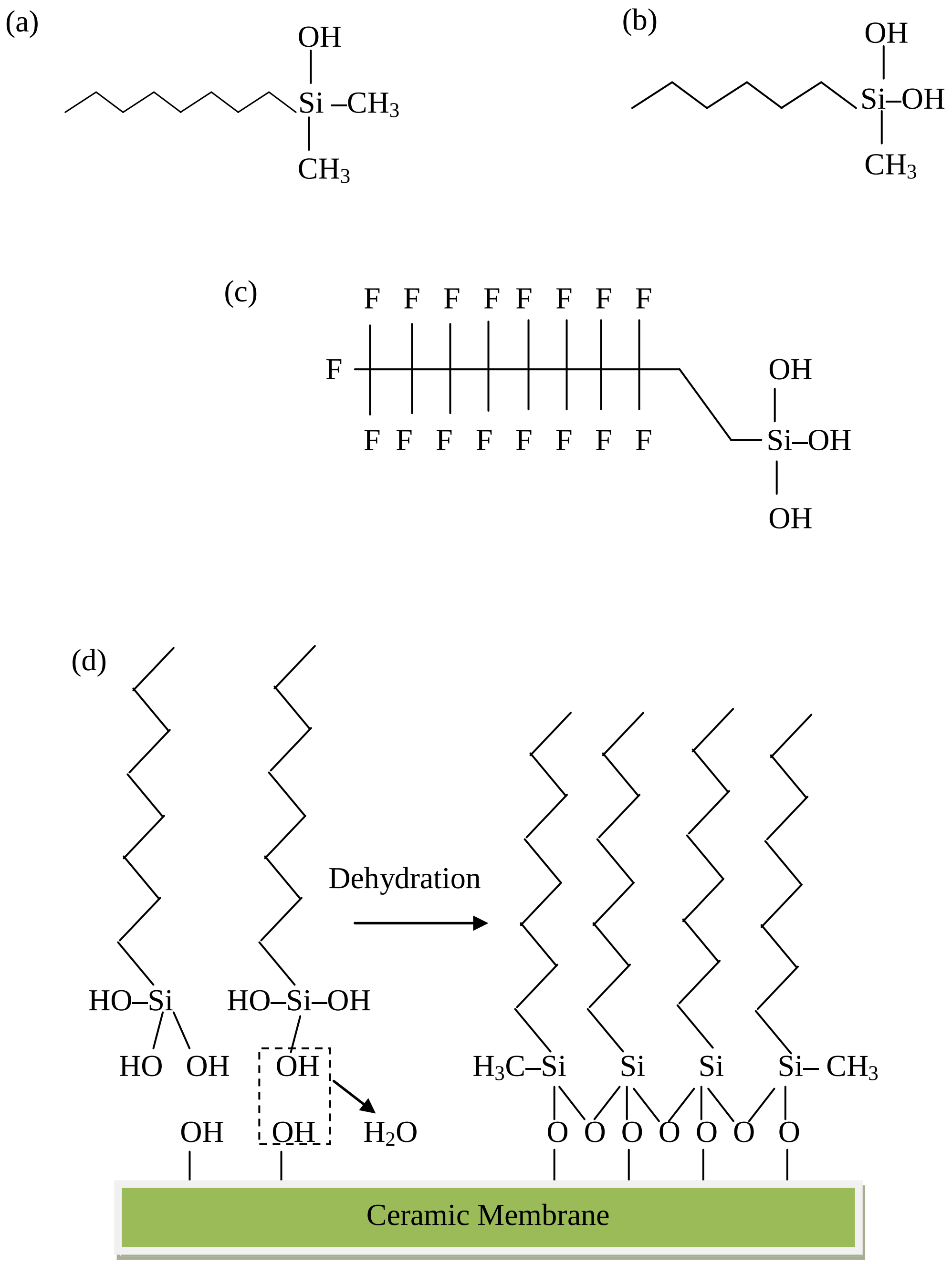


Figure 2.2: Hydrolysis of organosilane in solvent to form reactive organosilane solution.

There are three types of reactive organosilane molecules which have one, two or three silanol species as shown in Figure 2.3(a-c). Once the substrate is immersed in organosilane solution, the organosilane with reactive silanol species reacts with abundant OH groups present on the ceramic membrane. The organosilane molecules will be chemisorbed on the ceramic surface, resulting in hydrophobic surface (Lu *et al.*, 2009; Kujawski *et al.*, 2007; Herrmann, 2005; Picard *et al.*, 2004; Sugimura, 2002). Organosilane with a single –Si–OH species results in low molecular density of hydrophobic layer on the membrane, which is due to the steric hindrance between the methyl groups ($–CH_3$) of adjacent molecules. Organosilane with two or three –Si–OH species usually forms hydrophobic complex (Raza *et al.*, 2010; Xiameter, 2009b). After reacting with OH groups on the ceramic, the excessive Si–OH of the silane further reacts with adjacent Si–OH groups forming a Si–O–Si bond as shown in Figure 2.3(d) (Lu *et al.*, 2009; Kujawski *et al.*, 2007; Herrmann, 2005; Picard *et al.*, 2004; Sugimura, 2002). Strong linkage form among chemisorbed molecules leads to a closely packed; consequently forming a thin and uniform film. The hydrophobic surface is both chemically and mechanically stable due to strong immobilization of the molecules on the substrate, resulted from chemical bonding and presence of intermolecular attraction interactions (Sugimura, 2002;Sugimura, 2000).


(a)
OH
Si –CH3
CH3
(b)
OH
Si–OH
CH3
(c)
F F F F F F F F
F
F F F F F F F F
OH
Si–OH
OH
(d)
HO–Si
HO OH
HO–Si–OH
OH
OH OH
H2O
Dehydration
H3C–Si Si Si Si– CH3
O O O O O O O
Ceramic Membrane

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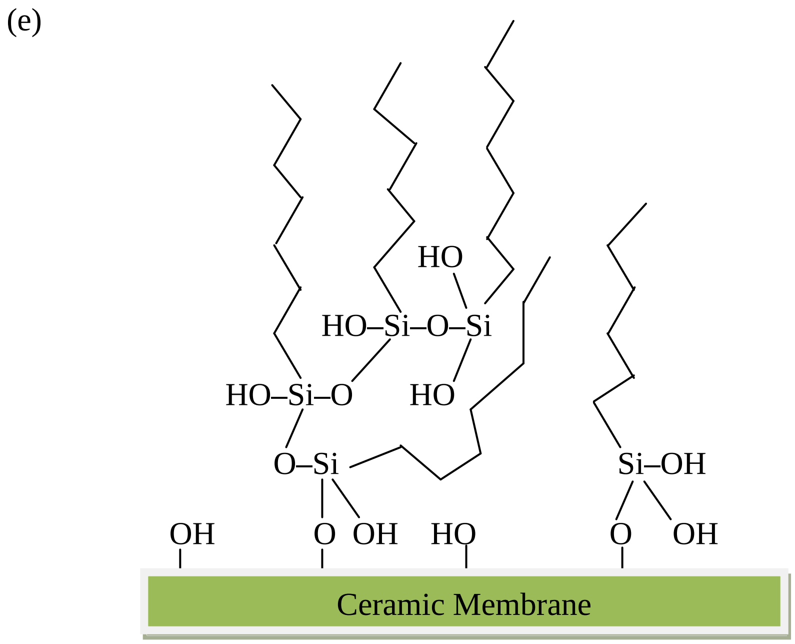

Figure 2.3: Types of reactive organosilane molecules and reaction on the membrane; (a) single –Si–OH, (b) double –Si–OH, (c) triple –Si–OH (d) formation of hydrophobic surface from complex organosilane molecules on ceramic membrane and e) vertical polymerization of organosilane on membrane.

Beyond intermolecular reaction for hydrophobic monolayer, poly-condensation reaction results in formation of gigantic organosilane molecules (Raza *et al.*, 2010; Lu *et al.*, 2009; Fadeev and McCarthy, 2000). Formation of the complex organosilane monolayer molecules (Figure 2.3(d)) only occurs between chemisorbed organosilane and free –Si–OH species. Poly-condensation reactions among the reactive organosilanes molecules are initiated by the water-sensitive silane groups. Effect of the condensation reactions among the silanols is shown in Figure 2.3(e), leading to formation of uneven thickness of organosilane layer and hydrophobicity. The grafting session has to be conducted under nearly water free condition with nitrogen flush (Vargas-Garcia *et al.*, 2011; Raza *et al.*, 2010), argon atmosphere (Krajewski *et al.*, 2006) or reflux at 65 ^{o}C (Cerneaux *et al.*, 2009).

Besides organosilane, vegetable oil can be used as grafting agent. Vegetable oils are relatively cheaper, available in large quantity, organic and most abundant (Petrovic, 2008; Hablot *et al.*, 2008; Javni *et al.*, 2003). Vegetable oils have been used to due few reasons such as low moisture absorption, high thermal stability and rich molecular design flexibility (Meshram *et al.*, 2013; Taşdelen-Yücedağ and Erciyes, 2013; Romero *et al.*, 2006; Aigbodion and Pillai, 2000). Lipid consists of fatty acid with long chains of mono and poly unsaturated acids. Lipid solution is another choice of grafting agent to prepare hydrophobic ceramic membrane. Chemical structure of the fatty acid consists of –COOH group which reacts with OH group of the ceramic substrate.

The lipid solution is prepared by mixing oil with solvent at a specific ratio. Selection of solvent, oil and concentration of the lipid solution are the few factors that affect the membrane properties. Romero *et al.*, (2006) used less than 14 %w/w of corn oil in dichloromethane to produce hydrophobic ceramic tubular membrane in order to concentrate aqueous solution. Although, lipid grafting is simple, economical and environmental friendly as no hazardous chemical is used, but it is not widely practised as it is limited to certain oil. Moreover, natural oil may be degradable for corrosive medium.

The achievement of organosilane or lipid grafting to produce hydrophobic membrane is affected by several factors; concentration of the grafting solution, OH group on the ceramic membrane, grafting duration, grafting numbers and surface roughness. The concentration of the grafting is representing the amount of reactive molecules reacting with the abundant OH groups on the ceramic membrane. However, the reaction is limited by the amount of OH on the ceramic membrane. Highly concentrated of grafting solution causes high production cost as organosilane is an expensive chemical. Even though lipid solution is easily found and low price, but high lipid concentration of more than 25 %w/w caused the membrane to be plugged and impermeable (Romero *et al.*, 2006). Grafting duration is relatively crucial in achieving maximum reaction between silanol or fatty acid and OH during the grafting process. In addition, superhydrophobic ceramic membrane could be developed by repeating the organosilane grafting process as supercomplex molecules shown in Figure 2.4. Formations of needle structures were observed on superhydrophobic ceramic membranes (water contact angle 164.53 ^{o}) surface after four times of fluoroalkylsilane (FAS) grafting. However, the needle structures could cause membrane pore shrinkage and consequently introducing higher resistance for mass transfer (Lu *et al.*, 2009). Multiple grafting encouraged the formation of supercomplex FAS molecules on the superhydrophobic alumina membrane particle and surface. Number of grafting should be controlled in order to produce hydrophobic ceramic membrane with low resistance.

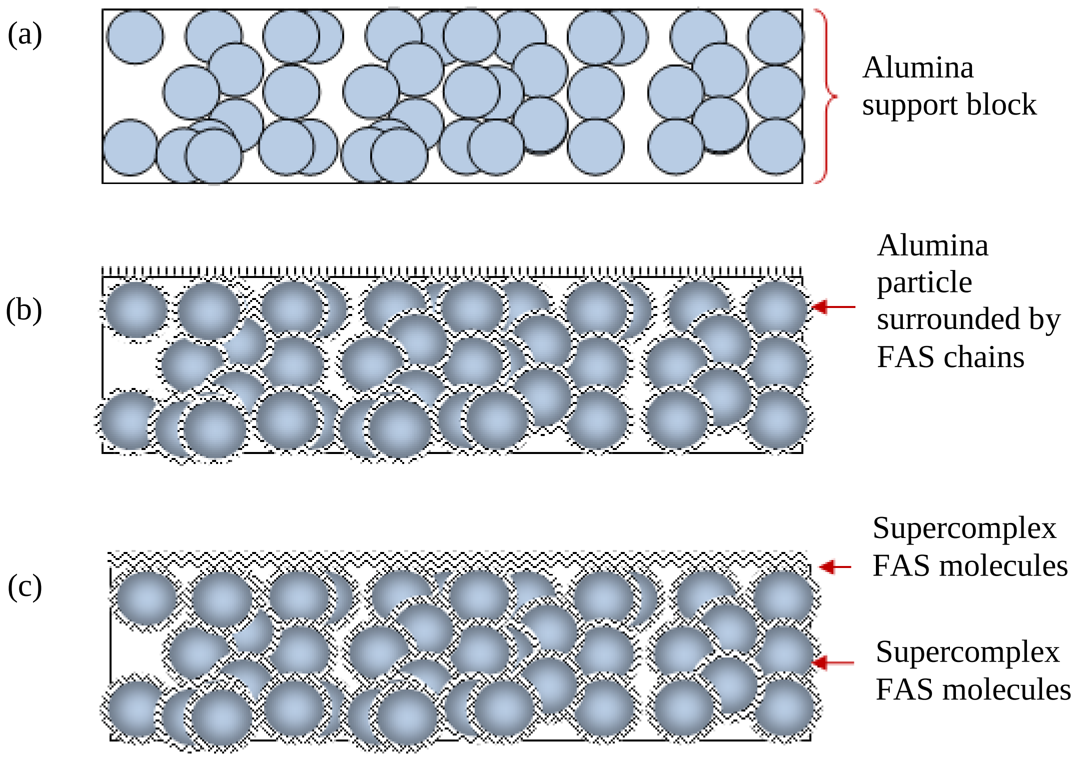

Figure 2.4: FAS grafting on hydrophilic alumina membrane into hydrophobic alumina membrane; (a) unmodified alumina membrane (b) single FAS grafting on alumina membrane (c) superhydrophobic alumina membrane after multiple FAS grafting processes.

2.1.1.2 Vaporization of organosilane compound

Chemical vapour deposition (CVD) is a frequently used technique in material-processing technology involve applying solid thin-film coating to surface (Vlassiouk *et al*., 2013; Xu and Yan, 2010; Sugimura, 2002). CVD involves the chemical reactions of gaseous reactants on or near the vicinity of a heated substrate surface. This atomistic deposition method can provide highly pure materials with structural control at atomic or nanometer scale level (Choy, 2003). Membrane grafting by using CVD method is alternative technique to produce hydrophobic membrane besides immersion in organosilane solution. Similar reaction between reactive organosilane and OH groups on the ceramic membrane occurs as mentioned earlier (section 2.1.1.1). But for this technique, heat should be applied to vaporize the organosilane and requires only a small quantity of solvent. There are few factors should be considered in this method: type of organosilane, concentration of the organosilane, boiling point of the solution (solvent and organosilane), volume of closed vessel and duration of grafting.

The reactive organosilane and the ceramic membrane are placed in a sealed container which is later heated in an oven at the boiling point of the organosilane for several hours (Figure 2.5). The reactive organosilane vapor reacts with the OH group on the ceramic membrane to form hydrophobic ceramic membrane. Appropriate size of the closed vessel and arrangement of the ceramic membrane samples are significantly crucial to maximize the reaction between the organosilane vapor and the ceramic membrane. Every organosilane molecules with different fuctional group has different chemical properties and reaction time, thus optimizing the grafting time should be taken into consideration. Sugimura (2000) in his research used three types of organosilane; n-octadecyltrimethoxysilane (ODS), n-(6-aminohexyl)aminopropyltrimethoxysilane (AHAPS) and fluoroalkysilane (FAS) to prepare organosilane self-assembled monolayers on ceramic surface. The liquid organosilane and the sample were placed together in a closed vessel in an oven at 100-150 ^{o}C. AHAPS and FAS required around an hour to achieve maximum contact angle around 62 ^{o} and 112 ^{o} respectively, but ODS required approximately 2 hours to achieve maximum contact angle of 105 ^{o}. FAS generates the highest water contact angle since it consists of hydrophobic groups; Si–C, C–C, C–O, $–CF_2–CH_2–$, $CF_2–CF_2–$ and $CF_2–CF3$ (Sugimura, 2002). The hydrophobic coating behaviour is affected by the length of fluorocarbon chain (Yim *et al.*, 2013). FAS molecules form fluorocarbon molecules which are more hydrophobic than the other two organosilane molecules. The deposition of tetramethoxysilane (TMOS), phenyltrimethoxysilane (PhTMS), and aminopropylmethyldiethoxysilane (APMDES) on alumina support resulted H_2/N_2 selectivity to be reduced but CO_2/N_2 selectivity to increase in gas separation (Han *et al.*, 2013).

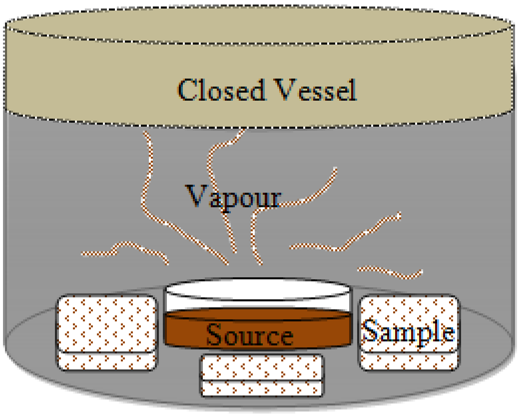

Figure 2.5: Vaporized organosilane in ceramic membrane grafting.

Although this method is easy to be applied, but there are several weaknesses should be considered. It is limited to certain organosilane compounds which has low boiling point. Furthermore, it requires a lot of energy and optimization via selection of the vessel size as well as sample arrangement is difficult. Besides proper safety precautions and proper handling are required since organosilane is toxic.

2.1.2 Morphological and chemical modification

Surface energy and roughness are two considerable factors that could determine superhydrophobic feature. The highest water contact angle is only about 110 ^{o} after direct gratfing of organosilane or lipid on a smooth ceramic surface using agents with low surface energy. Superhydrophobicity on smooth surface only could be achieved by multiple grafting processes as described earlier (section 2.1.1.1). However, the superhydrophobic ceramic membrane produced via multiple grafting might have higher membrane resistance and limited applications (Vargas-Garcia *et al.*, 2011; Noack *et al.*, 2000). Many researchers suggested that the enhancement of surface roughness could greatly improve membrane hyrophobicity greatly where a water contact angle more than 150 ^{o} (Han *et al.*, 2012; Feng et al., 2012; Fang, 2009; Taurino *et al.*, 2008; Zhang *et al.*, 2008; Tadanaga *et al.*, 2003). The presence of roughness improved the water contact angle as explained in Wenzel's (Jun *et al.*, 2008) and the Cassie-Baxter models (Cassie and Baxtie, 1994).

A few reseachers introduced surface errosion using chemical such as NaOH to improve surface roughness and then grafted the rough surface with poly(dimethysiloxane) vinyl terminated, fluoronane per or tridecafluoroctyltriethoxysilane (Lu *et al.*, 2009; Guo *et al.*, 2006). However, this method depends on the material characteristics and the presence of impurity (Dong *et al.*, 2011; Hsieh, 1996; Burggraaf, 1996). The presene of silica in porous alumina support caused high erosion rate and rapid mass loss in NaOH during surface erosion (Dong *et al.*, 2011). Besides that, erosion could be strongly localized and caused internal microstructure alteration (Burggraaf, 1996). Due to these limitations, sol-gel method was proposed to create great roughness without using any corrosive solvent (Han *et al.*, 2012; Fang *et al.*, 2009; Zhang *et al.*, 2009; Tadanaga *et al.*, 2003; Tadanaga *et al.*, 1997a).

Sol is referred to a colloidal suspension of solid particles in a liquid. A colloid is a suspension in which the dispersed phase is so small (1-1000 nm) that gravitational forces are negligible and interactions are dominated by short-range effects, like van der Waals attraction and electrostatic forces resulting from surface charges. A gel is referred to a porous, three-dimensional and continuous of solid network surrounding a continuous liquid phase. Sol-gel method is the most common approach of creating ceramic thin films. The high and great interest in sol-gel synthesized material is contributed by few reasons. Great porous materials and nanocrystalline material can be produced with controlled pore size, porosity and desired surface feature. Moreover, sol-gel method is used to enhance roughness on superhydrophobic film. Generally, there are two routes used to synthesis alumina sol; colloidal route (in aqueous medium) and polymeric routes (in organic solvent) which are able to produce porous materials (Guizard, 1996). Figure 2.6 shows the sol-gel routes. The preparation of a sol is commonly started with metal alkoxides (as precursor) which is classified as metalorganic compounds. The general formula for metal alkoxides is written in equation stated below:

$$M(OR)_x \tag{2.1}$$

where M is a metal, R is an alkyl group and x is the valence state of the metal (for example x = 4 for Si, Zr and Ti and x = 3 for Al).

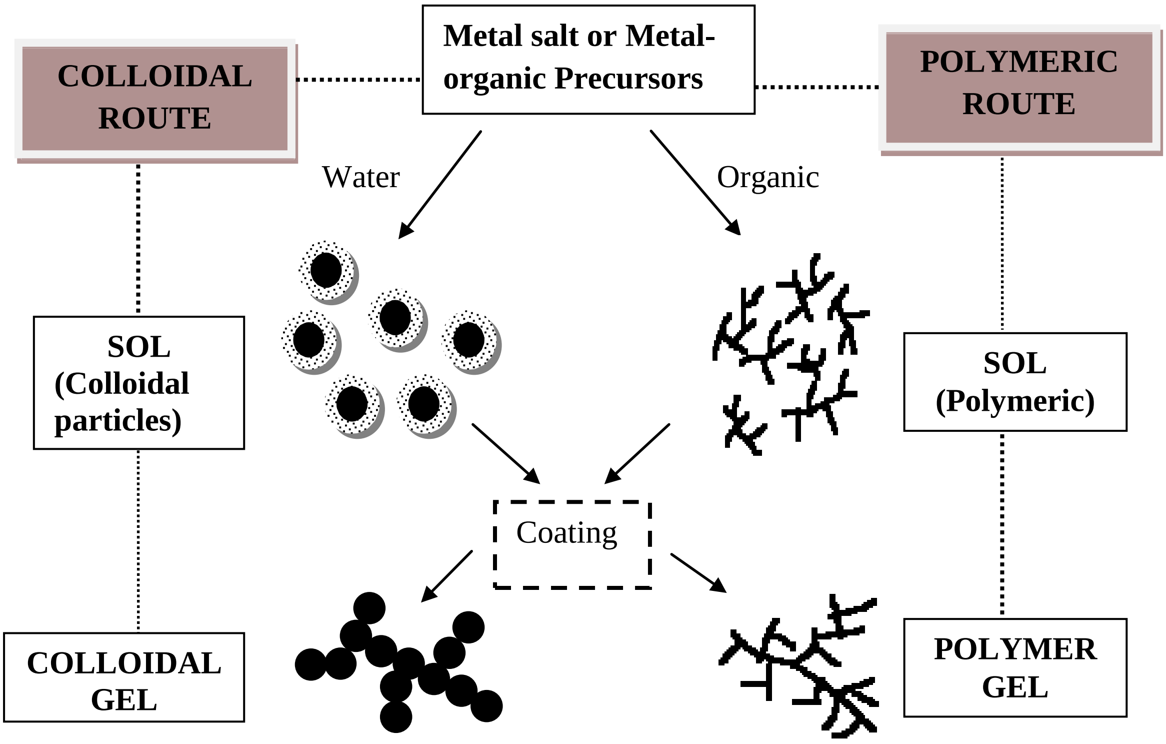

Figure 2.6: Preparation of sol-gel.

In the colloidal sol route, a metal alkoxides dissolved in alcohol is hydrolyzed in excess of water. In the hydrolysis reaction, OH attaches to metal atom while alcohol was released at the same time. Condensation reactions between two hydroxylated metal species leads to the formation of metal-oxygen-metal bonds (M-O-M) and the release of water molecule as a by product. Hydrolysis causes a dispersion of colloidal particles in a liquid then; gel is produced after condensation and polymerization reaction. The colloidal sol route can produce mesoporous or microporous ceramics. Removals of the pore liquid under hypercritical conditions without collapse network produce an aerogels. Drying process under ambient conditions cause pore shrinkage, and leading to the formation of xerogel. For instance, the overall process for the preparation of ceramic membrane using colloidal route can be summarized as shown in equations below (Kobayashi *et al.*, 2005; Niederberger, 2009):

Hydrolysis:

$$M-OR \quad + \quad 4\,H_2O \quad \rightarrow \quad M-OH \quad + \quad ROH \tag{2.2}$$

$$Si(OC_2H_5)_4 \quad + \quad 4\,H_2O \quad \rightarrow \quad Si(OH)_4 \quad + \quad 4C_2H_5OH \tag{2.3}$$

Tetraethyl orthosilicate water silicon hydroxide ethanol

Condensation by oxolation:

$$M-OH \quad + \quad M-OH \quad \rightarrow \quad M-O-M \quad + \quad H_2O \tag{2.4}$$

$$Si(OH)_4 \quad + \quad Si(OH)_4 \quad \rightarrow \quad 2SiO_2 \quad + \quad 4H_2O \tag{2.5}$$

Silicon hydroxide silicon oxide water

Condensation by alkoxolation:

$$M-OR \quad + \quad HO-M \quad \rightarrow \quad M-O-M \quad + \quad ROH \tag{2.6}$$

$$Si(OC_2H_5)_4 \quad + \quad Si(OH)_4 \quad \rightarrow \quad 2SiO_2 \quad + \quad 4C_2H_5OH \tag{2.7}$$

The colloidal sol-gel route involves fast hydrolysis reaction and the formation of condensed species from aqueous solutions of inorganic salts. This method highly depends on processing conditions such as the pH, increasing the temperature, mixing method, rate of oxidation, nature and concentration of anions. However, the colloidal sol-gel chemistry is quite complex in order to provide good reproducibility due to few factors; high reactivity of the metal oxide precursors towards water, double role of water as ligand and solvent, and the large number of reaction parameters that have to be strictly controlled (hydrolysis and condensation rate of the metal oxide precursors, pH, temperature, method of mixing, rate of oxidation,the nature and concentration of anions). The presence of counter anions in final product contribute to the undesired problems which eventually affects the morphology, structure and chemical composition of final solid phase. These problems are due to the anions that able to coordinate the metal ions into a new molecular precursor with different reactivity in hydrolysis and condensation.

In the colloidal sol-gel routes, metal alkoxides are used as precursor, and their chemical transformation into the oxidic system involves hydrolysis and condensation reactions. The presences of water molecules supply oxygen in the formation of the oxidic compound. In the polymeric so-gel routes, the reaction of precursor occurs in an organic solvent without or minimum of water, and followed by appropriate aging. This sol-gel preparation route is applied to produce microporous and ultraporous materials. The oxygen is supplied by solvent (alcohol, ether or acetylaetonates) or precursor (alkoxides or acetyacetonates) to produce metal oxide gels. The main condensation steps in nonaqueous sol-gel processing form a metal-oxygen-metal bond ($\mathrm{M-O-M}$). Example for the general reaction mechanism is presented as below (Niederberger, 2009):

Aldo condensation reactions:

$$\underset{\text{alkoxide}}{\mathrm{2M-OR}} + \underset{\text{propanone}}{\mathrm{2O=C(CH_3\,)_2}} \xrightarrow{\mathrm{-2ROH}} \mathrm{M-O-M} + \underset{\substack{\alpha,\beta\text{-unsaturated}\\ \text{carbonyl compounds}}}{\mathrm{O=C(CH_3)CH=C(CH_3)_2}} \tag{2.8}$$

The aqueous method involves peptization process in hydrolysis of precursor in excess of water. Aluminium-tri-sec-butoxide (ASB) has been widely used as precursor of Al_2O_3. The ASB molecules are undergone sufficient hydrolysis in water and the formed Al_2O_3 precipitates are peptized into colloidal particles. Peptization process is a popular approach in the preparation of Al_2O_3 sol-gel material since it has been identified as being capable of producing the smallest average pore size and porosity. The molar ratio of ASB to water was fixed around 1:100 to get stable sol with an acceptable lifetime. The non-aqueous method involves the polymerization and polycondensation reaction of ASB molecules in organic medium with a small amount of water presence.