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by Adi Darmawan

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CHAPTER 4

Microporous Silica Membrane: Structure, Preparation, Characterization, and Applications

Julius Motuzas[*], **Adi Darmawan**[†], **Muthia Elma**[‡], **David K. Wang**[§]

[*]The University of Queensland, FIM²Lab-Functional and Interfacial Materials and Membranes Laboratory, School of Chemical Engineering, Brisbane, QLD, Australia, [†]Department of Chemistry, Diponegoro University, Semarang, Indonesia, [‡]Chemical Engineering Department, Lambung Mangkurat University, Banjarbaru, Indonesia, [§]The University of Sydney, School of Chemical and Biomolecular Engineering, Sydney, NSW, Australia

1 Introduction

In 1989, Uhlhorn et al. (1989) reported the possibility to sieve gases using silica if it is formed as a thin film or membrane. Since then, using silica in the membrane configuration has become one of the most researched materials in inorganic porous membrane preparation. Many efforts have been focused on optimization of preparation venues, development of characterization methods, and investigation of the potential niches of application of silica membranes. Since the 1990s, methyl silica, silica-containing carbon templates, metal oxide/silica, and organosilica structures have been investigated in membrane configurations. The thermal treatment has also evolved significantly, reducing the preparation time from days to an hour without sacrifice of membrane quality. Considering its application in gas separation, there has been a significant increase in knowledge on hydrogen purification (Kanezashi et al., 2013; Khatib and Oyama, 2013; Miyajima et al., 2012; Jasti et al., 2012) and carbon dioxide (Yildirim and Hughes, 2003; Chew et al., 2010) removal. Also, potential applications such as desalination and pervaporation have been explored using silica membranes. Within this chapter, each of the basic research fields previously mentioned will be discussed in more detail.

2 Silica Formation by a Sol-Gel Method

Sol-gel-derived ceramic engineering has been widely applied in the production of ceramics of various porosity and morphology (Brinker and Scherer, 1990a). The ability to form thin film coatings from a variety of ceramic precursors is of great interest for silica, titania, and

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alumina membrane researchers (Brinker and Scherer, 1990a; Brinker et al., 1988, 1985; Larbot et al., 1989; Klein and Gallagher, 1988; Anderson et al., 1988; Gieselmann et al., 1988; Moosemiller et al., 1989). Such flexibility and versatility are important considerations for the fabrication of mesoporous intermediate layers and microporous selective layers. For silica membranes, a silica sol-gel process is carried out using tetraethyl orthosilicate (TEOS), which is the most widely utilized silica monomer for material development. This silica precursor is commercially available and offers the ease of chemical processability for synthesizing a high-quality silica layer with well-defined pore sizes for membrane technology. The chemistry involves the hydrolysis of functionalized silica precursors into building blocks of monomers and the condensation (polymerization) of these monomers into an interconnected network or gel. These reactions are depicted in Eqs. (1)–(3):

$$\equiv \mathrm{Si}-\mathrm{OR}+\mathrm{H_2O} \underset{\text{Esterification}}{\overset{\text{Hydrolysis}}{\rightleftarrows}} \equiv \mathrm{Si}-\mathrm{OH} \tag{1}$$

$$\equiv \mathrm{Si}-\mathrm{OR}+\mathrm{HO}-\mathrm{Si}\equiv \underset{\text{Alcoholysis}}{\overset{\text{Alcohol Condensation}}{\leftrightarrows}} \equiv \mathrm{Si}-\mathrm{O}-\mathrm{Si}\equiv +\mathrm{R}-\mathrm{OH} \tag{2}$$

$$\equiv \mathrm{Si}-\mathrm{OH}+\mathrm{HO}-\mathrm{Si}\equiv \underset{\text{Siloxane Hydrolysis}}{\overset{\text{Water Condensation}}{\leftrightarrows}} \equiv \mathrm{Si}-\mathrm{O}-\mathrm{Si}\equiv +\mathrm{H_2O} \tag{3}$$

where OR is a hydrolyzable alkoxy group bonded to the silicon atom.

In Eq. (1), hydrolysis reaction in the forward direction involves the functional alkoxy groups of the TEOS precursor. In this step, the alkoxy groups undergo hydrolysis in the presence of water or moisture to form the hydroxyl groups bonded with the central silicon atom and produces the alcohol (R-OH) as the byproduct. This step transforms the TEOS precursor into a monomer functionalized by the silanol group (Si-OH). Then, condensation reactions proceed in the forward direction via alcohol or water condensations, where the silanol groups react with either an alkoxy group (Eq. 2) or another silanol group (Eq. 3) to produce siloxane bonds (Si—O—Si) along with the alcohol or water byproducts, respectively. Because TEOS is not soluble in water, the sol-gel chemistry will require a mutual cosolvent such as alcohol to maintain constant solution homogeneity to achieve a fast reaction transfer process (Brinker and Scherer, 1990b). Very recently, this conventional school of thought was challenged when a silica sol-gel process was carried out heterogeneously at the interface between two immiscible phases (Wang et al., 2015a). This work revealed that the silica monomers could be formed at the interface of the two layers (alkoxysilane precursor layer and the cosolvent layer) followed by the migration of the silanol groups into the cosolvent phase. Therefore, the flexibility and processability of sol-gel chemistry for porous ceramic membrane fabrication are further attested by offering reaction opportunities even in phase-separated systems with predictable properties and functionalities.

An important factor controlling the degree of a sol-gel process is the molar concentration of water to silicon (H_2O:Si). It is widely reported that sol-gel chemistry should be performed with a relatively low H_2O:Si ratio (5–8) to control the relative rates of hydrolysis and condensation reactions to minimize the reverse reactions. According to the generally known Le Châtelier Principle, because water is a reactant but also one of the byproducts, any excess at the beginning of the sol-gel reaction will cause the equilibrium to shift in the reverse direction on one hand. On the other hand, when water concentration far exceeds the cosolvent (alcohol) or alkoxysilane concentrations, phase separation will occur as ethanol will preferentially stay miscible with water than in alkoxysilane (Wang et al., 2015a). Therefore, to achieve a homogeneous solution for silica thin film, a low H_2O:Si molar ratio is highly recommended (de Vos and Verweij, 1998; Diniz da Costa et al., 2002).

Furthermore, pH of the sol solution and the isoelectric point (IEP) of the silica species are critical considerations for any sol-gel process because the IEP of each precursor can vary slightly. For silica species, IEP is around pH 2, where it is known as the point of zero electrical charge on the particles (Iler, 1979). At this point, the silica particles are not interacting with each other through ionic forces. In contrast, when pH of the sol-gel solution is altered from below pH 2 (acidic) to above pH 12 (basic), chain growth of silica proceeds from an acid-catalyzed to a base-catalyzed sol-gel process, which undergo two separate morphological pathways; from a polymeric sol-gel route to a colloidal sol-gel route.

In addition to the reactants and products concentration, the sol-gel process can be further promoted/inhibited by changing precursor functionality, the molar ratio of alcohol to precursor, solvent type, catalyst species, pH of sol, and reaction temperature (Brinker et al., 1985; Estella et al., 2007; Polevaya et al., 1995; Brinker, 1988). As shown in Fig. 1, recent studies have demonstrated the importance of these parameters in controlling the process of sol-gel reactions with respect to the types of material morphologies (Wang et al., 2015a, 2017, 2014, 2015b; Elma et al., 2013; Wang, 2016).

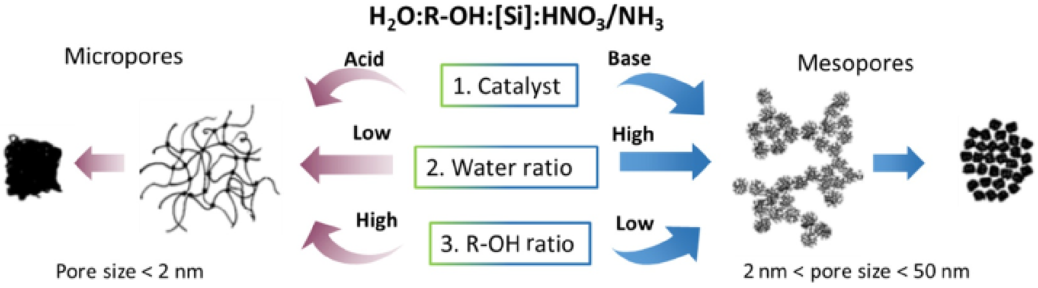

Fig. 1

The effect of sol-gel reagent molar ratio and catalyst types on silica morphology and texture.

To produce the final membrane film, the sol-gel is required to be coated onto a smooth porous support, dried, and then calcined at a high temperature in the range of 400–600°C, depending on the silica precursor types and final membrane morphology. In this second step, the drying-calcination protocol is very important in controlling the formation of the membrane layer as it determines the final membrane pore sizes, which is a critical criteria of membrane separation applications.

The heating process is typically studied in terms of the heating rate, the calcination temperature, and the heating duration followed by the cooling rate, all of which govern the densification process of the silica gel network and thus the final pore size distribution (Brinker et al., 1985). Hence, to prepare a high-quality silica membrane, the final morphology of the membrane is a function of the hydrolysis and condensation reaction conditions, in the first step, followed by the drying-calcination conditions. As depicted in Fig. 1, depending on the sol-gel reaction and processing parameters, there are two main silica morphologies with respect to their pore sizes. First, the colloidal route consists of dense but discrete nanoparticles that are well-condensed in silica gel networks with siloxane functionality. The colloidal process is typically promoted by high water, low cosolvent (R—OH) molar ratios and the presence of a base to produce the colloid, branched gels. The silica sol is then coated onto a polished macroporous support where the nanoparticles continue to polymerize to form an interconnected network in which the membrane pore sizes are governed by the voids existing between the nanoparticles, and thus, the final morphology is commonly mesoporous.

Second, the polymeric route consists mostly of linear silica polymeric chains with predominately silanol functionality, which are afforded by using low water and cosolvent molar ratios and the presence of an acid. The silica sol is then coated onto a support with the smooth intermediate layer. During drying/calcination, it proceeds with some degree of condensation to form a loosely interconnected silica gel where the pore sizes are governed by the voids between the polymer chains and are therefore typically microporous.

It is widely recognized that porous ceramic membranes with pore sizes in the mesoporous range (2–50 nm) could be used for nanofiltration and ultrafiltration for liquid separations. These membranes are generally created by the colloidal route using various ceramic sols from alumina, titania, zirconia, and silica to form the selective mesoporous layers. To be efficacious for gas separation membranes, pores sizes must be in the molecular-sieving regime as the separation is governed by size-exclusion on a molecular scale (i.e., less than 1 nm) (de Vos and Verweij, 1998; Diniz da Costa et al., 2002). The polymeric sol-gel route is ideal for this purpose (Diniz da Costa et al., 2002; Verweij, 2003).

3 Membrane Fabrication

Membrane fabrication is a complex procedure involving sol preparation, dip-coating, drying, and calcination steps. In this section, those steps and their importance on membrane quality will be presented and compared for different types of silica membranes.

3.1 Dip-Coating and Calcination

The dip-coating process is the most common layer deposition on a substrate technique in sol-gel technology. The process consists of immersion of the substrate into the sol prepared by sol-gel method, withdrawal from the sol, and consolidation by drying and thermal treatment (Puetz and Aegerter, 2004; Brinker et al., 1991) (Fig. 2). In the dip-coating process, outcomes such as thickness can be controlled by the speed of the support withdrawal rate and viscosity by the solution. For example, thicker films are formed using faster withdrawal speed. Generally, the withdrawal speed ranges from 1 to 10 mm s^{-1} (Faustini et al., 2010).

The solvent evaporation speed and surface tension are also essential factors in the dip-coating process. For instance, alcohols are usually used in silica preparation. They have a low surface tension, which prevents de-wetting and promotes fast evaporation (Faustini et al., 2010). The consolidation stage represents a transition with concurrent processes of draining, evaporation, and hydrolysis. When the volatile solvent is employed during the coating process, the complete transition will pass in only a few seconds or less and form a film from nonvolatile components of the sol (Puetz and Aegerter, 2004).

The coated membranes are submitted for calcination. The general purpose of calcination is to condense the silica structure. The resulting properties of the formed membrane strongly depend on the calcination conditions such as temperature, atmosphere, and duration. Calcination in the air is one of the most common methods of silica membrane preparation if complete removal of all organic groups is desired. The primary factor that influences this method is calcination temperature. A higher temperature results in a higher degree of silica network condensation and densification of the structure.

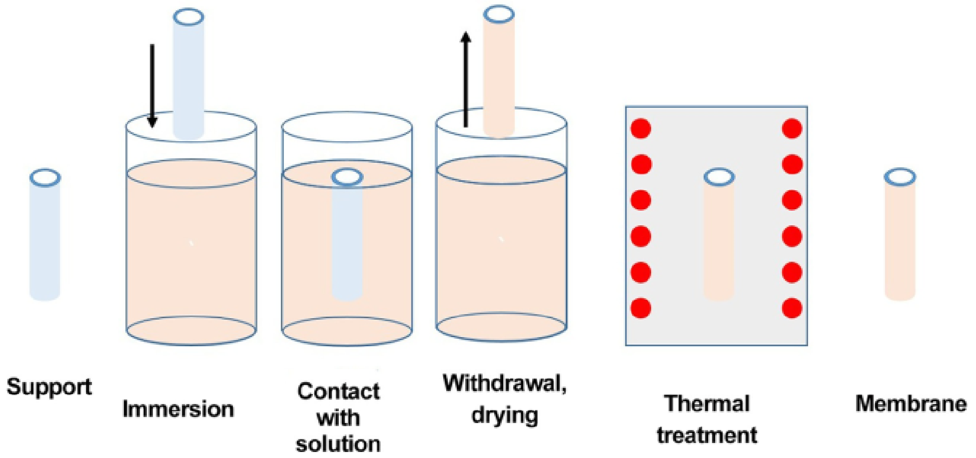

Fig. 2
Membrane preparation procedure from support to the operational membrane using the dip-coating approach.

Calcination under inert gas aims to prevent the combustion of organic groups (Nagasawa et al., 2018) or to form carbon from the organic group such as covalent templates (Wijaya et al., 2009), surfactants (Ladewig et al., 2011), or triblock copolymers (Elma et al., 2015a; Chua et al., 2015a, b). The presence of carbon or organic groups increases the hydrostability properties of the silica (Duke et al., 2006). Vacuum-assisted calcination is also widely used in silica membrane preparation. The purpose of both methods is either to retain organic groups or form carbon within the materials. It was also observed that the carbonization conditions and change the structure of the materials. For example, silica materials prepared under N_2 have higher surface area yet retain a similar total pore volume and pore diameter when compared to the material prepared under vacuum (Elma et al., 2015a). Calcination under steam was reported by Kanezashi et al. (Kanezashi et al., 2018), however this calcination method is rarely used.

3.2 Rapid Thermal Treatment

Conventionally, the time required for thermal treatment becomes an obstacle in the preparation of the silica membrane. Although the sol-gel process requires a short period of time (generally up to 3 h), the process of silica membrane preparation takes a long time. For example, to make a thin layer with a calcination temperature of 600°C and a ramp rate of 2°C min^{-1} will require 12 h to get to the target. One asymmetric membrane consists of several layers, therefore, for one membrane module, it may take several days until production is completion. Therefore, to accelerate this process, researchers (Kappert et al., 2012; Schillo et al., 2010) tried what is called a *rapid thermal processing technique* (RTP) with a heating rate of up to 100°C s^{-1} (Wang et al., 2014). They performed a synthesis of silica membranes with rapid calcination, in which each membrane layer was heated for 1 h at 600°C without stepping of temperature. The later process allowed the membrane fabrication process (including sol-gel, coating process, and calcination) to be finished in 1 day. Kappert et al. (2012) performed a comparative study between conventional and rapid calcined methods, showing a drastic reduction in time needed to form the silica membrane from 41 h to 1 h at most. The latter reports are direct contradictions to previous claims that the process of forming a thin film must be done with a low-temperature ramp rate to produce a noncracked membrane. In addition to reducing the manufacturing process, RTP can enhance the crystallization process (Motemani et al., 2011; Siemer et al., 2001) and facilitate the rapid manufacture of films with micrometers.

4 Membrane Characterization

Since the discovery of silica membranes, various indirect and direct analysis methods have been applied in the characterization of their structure, composition, morphology, and performance. For example, Fourier transform infrared (FTIR) is one of the indirect characterization methods providing information on the presence of the groups within the silica network (Elma et al., 2015a; Chua et al., 2015a). FTIR spectra and deconvolution curves

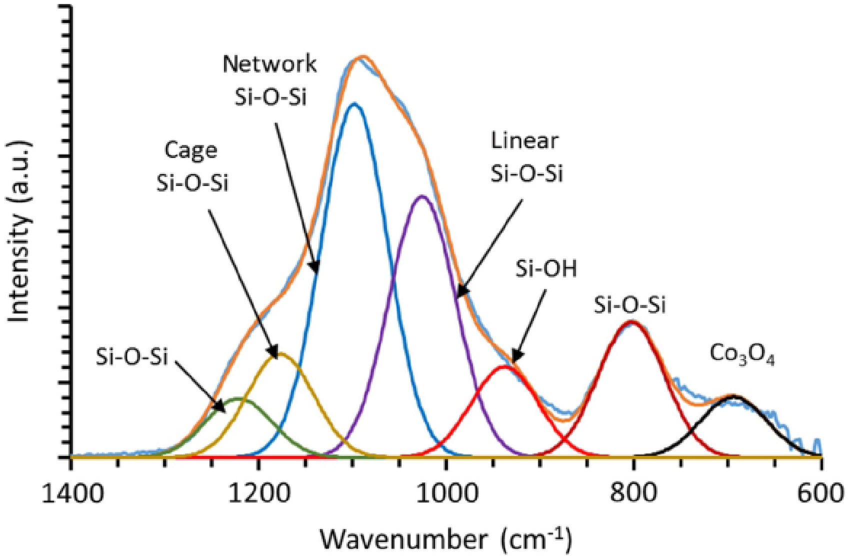

Fig. 3

Deconvolution of cobalt oxide/silica membrane prepared with a sol-gel method and thermally treated at 630°C in air.

of cobalt oxide/silica materials are presented in Fig. 3. Therein, the bands at 800, 1025, 1089, 1179, and 1225 cm^{-1} are attributed to different types of interaction of Si—O—Si bonds with infrared radiation within the silica network. Meanwhile, the bands at 670 cm^{-1} and 950 cm^{-1} are accordingly attributed to Co—O in Co_3O_4 oxide and silanol bonds (Si-OH) in silica, respectively (Elma et al., 2015a; Chua et al., 2015a).

A silicon nuclear magnetic resonance (^{29}Si NMR) is another attractive technique in determining the silicon to other silicon atom connectivity within the silica network. The analysis by ^{29}Si NMR reveals the degree of the silicon atom connectivity to other silicon atoms through an oxygen bridge in silica materials. The central silicon atom is usually called a T atom. There are five possible types of silicon atoms to have T_0, T_1, T_2, T_3, and T_4 connections in the siliceous systems (Fig. 4).

The highest branching would correspond to the central silicon atom connectivity to four other silica atoms. Meanwhile, T_0 is attributed to unbranched silicon atoms in the molecule or those having no other neighbors (for example, Si in TEOS). This type of analysis allows for determining the degree of the hydrolysis of the precursors during the sol-gel process and the cross-linking of the system.

Gas sorption is also widely implemented in silica material characterization as an indication of the porosity. This analysis allows quantitative characterization of the porosity accessible to the adsorptive gas, which is usually nitrogen. The major limitation of the technique is the size of

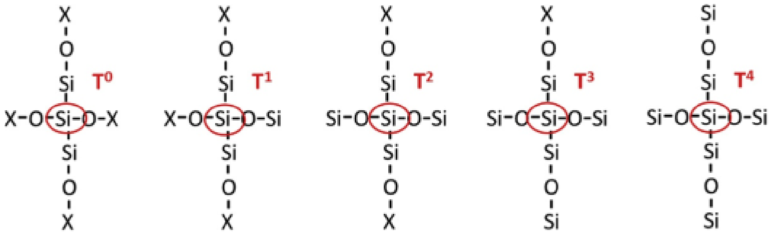

Fig. 4
Silicon atom position in silica networks.

the pores; the ultramicropores existing in silica are not accessible for nitrogen molecules. Thus this technique does not reveal the total porosity of the system but just the porosity of pores larger than the size of the adsorptive gas.

Comparing the membrane's characterization to bulk materials is even more challenging. The primary challenge is that the quantity of silica in the membrane is very little compared to that required for use by the bulk analysis techniques. The silica layers are formed from a small amount of the material, whereas the bulk analysis techniques require at least 0.1 g of material. Thus, the membrane characterization employing a scanning electron microscopy (SEM) is very attractive. The SEM allows accruing information on membrane thickness, surface morphology, and homogeneity (Fig. 5).

X-ray photoelectron spectroscopy (XPS) is a widely used analysis method in membrane and bulk materials characterization. XPS provides information on the membrane's chemical composition and thickness. For example, the evolution (profiling) of the chemical composition as a function of the membrane thickness can be determined (Fig. 6) (Ballinger et al., 2015).

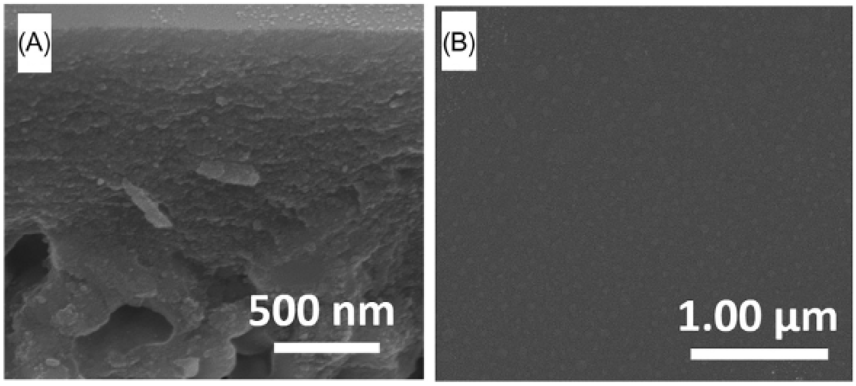

Fig. 5
Surface (A) and cross-section (B) of cobalt oxide-silica membranes prepared by sol-gel method and calcination in air at 630°C.

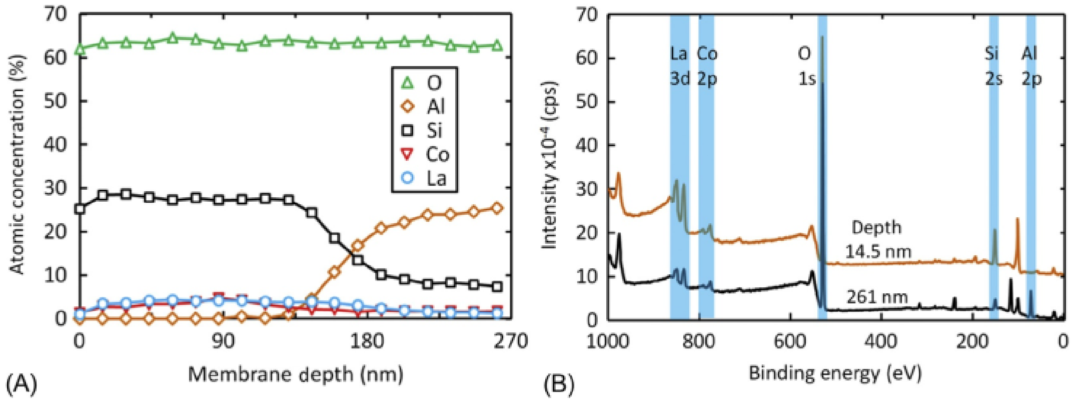

Fig. 6

XPS sputter profile through the La_5Co_{10} membrane (A) and spectra at 14.5 nm (+10^5 cps) and 261 nm (B).

The acquired data show that the concentration of silicon remains similar for the top 150 nm and starts to slowly decrease. The opposite tendency is observed in the aluminum case. Furthermore, an increase in aluminum and further decrease in silicon leads to the conclusion that the support becomes the major phase of the sample, and the silicon is infiltrated to its porosity. The intersection point at 170 nm can be attributed to the end of the top layer (silica membrane).

Regarding the dynamic characterization methods, gas permeation is the usual quality control approach applied in membrane preparation. The prepared membranes are submitted to pressured gas on one side, and the permeances (Π, mol m^{-2} s^{-1} Pa^{-1}) are measured on the other side of the membrane (Fig. 7).

He (0.26 nm), H_2 (0.289 nm), CO_2 (0.33 nm), and N_2 (0.36 nm) are the usual gases tested for membrane quality determination. The membrane ideal permselectivity (for example, $\alpha(He/CO_2)$) is defined as a ratio of the permeance (in moles or volume) of the smaller gas

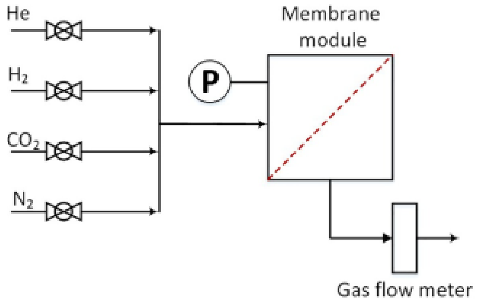

Fig. 7

Single gas permeation rig.

(Π(He)) over the larger (Π(CO_2)). The gas with the smaller kinetic diameter molecular size is expected to flow faster through the membrane compared to the larger if the membranes are selective (Yildirim and Hughes, 2003; Anderson et al., 1988; Gieselmann et al., 1988).

5 Membrane Application

Silica membranes application has ranged from pervaporation, gas separation, water vapor extraction from gas, and ammonia separation to desalination since the discovery of the silica membranes in the 1990s. From the gas separation, hydrogen extraction from gas mixtures has gained attention due to the invention of silica membranes. Meanwhile, silica membrane applications in desalination have been under investigation for just the last decade. The specific niches of application and the arising challenges from those applications of silica membranes will be the focus of following chapters.

5.1 Optimization of Silica Membrane for Gas Separation

Currently, silica membranes with attractive performance can be obtained either by chemical vapor deposition (CVD) (Nagano et al., 2008) or by the sol-gel process (Tsuru, 2008). Typically, H_2 permeance, and H_2/CO_2 and H_2/N_2 permselectivity values reported in the literature for the previously mentioned types of silica membranes are compared in Fig. 8. CVD silica membranes generally deliver high hydrogen selectivity (molecular sieving) but

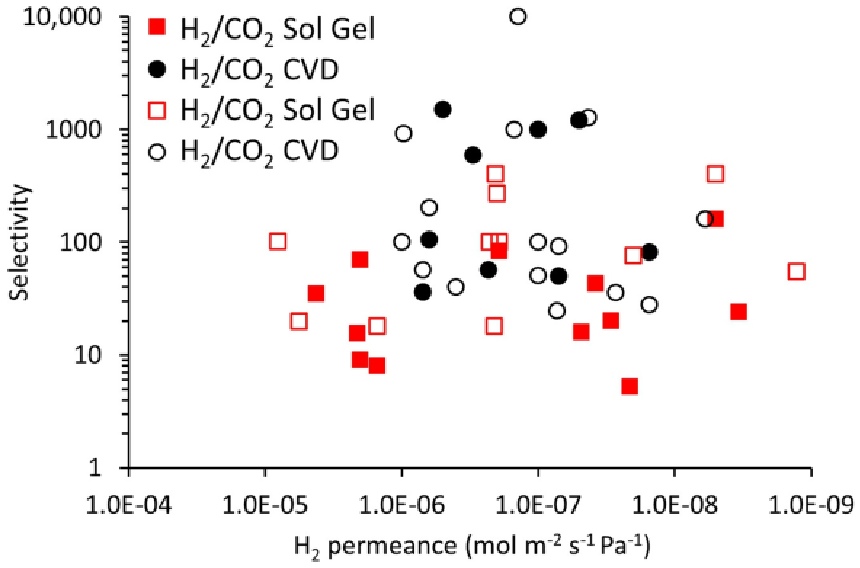

Fig. 8

Comparison of H_2/CO_2 and H_2/N_2 selectivities as a function of H_2 permeance through sol-gel and chemical vapor deposition (CVD)-derived silica membranes from the literature.

lower permeabilities compared to sol-gel derived membranes. These values are dependent upon the temperature, membrane thickness, and testing conditions. The sol-gel-derived membranes generally achieve lower selectivities but higher permeabilities, and are much easier to produce.

Although the silica membranes synthesized through sol-gel or CVD processes adequately demonstrate good permeability and selectivity, there are still many challenges to be resolved prior to the membrane's application. For example, high hydrogen permeance and selective separation of other gases, as well as the ability to maintain stability in hot steam conditions, are among the prerequisites for steam reforming (SR) and/or water gas shift (WGS) reactions. The initial approach was to improve hydrothermal stability in preparing high-performance microporous membranes by designing a silica structure containing less silanol using new silica precursors (e.g., organosilica), replacing conventional tetraethoxysilane (TEOS) or by the incorporation of hydrophobic alkyl groups into silica by co-condensation of tetraalkylsilane to improve hydrophobic properties and facilitate Si—O—Si bonds (Kanezashi et al., 2012; Moon et al., 2008; Li et al., 2011; de Vos et al., 1999; Castricum et al., 2008; Paradis et al., 2013). The use of membranes derived from organic silica precursors increases the thermal stability of membrane silica compared to conventional silica membranes. However, the gas selectivity of methyl-templated silica membranes is lower than that of pure silica and, therefore, is not as effective for H_2 separation from gaseous streams containing CO_2 and CO. Also, the use of organosilica membranes is limited to low temperatures of 300–350°C to avoid decomposition of organic groups (Kanezashi et al., 2012). At high temperature, the alkyl group included in the structure may oxidize to CO_2 and generate big pores, which are detrimental to the membrane permselectivity. However, these materials showed excellent hydrostability and are effective for pervaporation of organics (Campaniello et al., 2004). de Vos et al. (1999) used MTES as a silica matrix whereas the ligand methyl group was maintained in the silica matrix. Giessler et al. (2003) investigated the stability of silica membranes using MTES and surfactants as templates in the membrane preparation process and their application in the WGS reaction. Their work showed that, over time, the template silica membranes performed better, although initially, gas separation was lower. This was attributed to the slight pore-widening effect of the surfactants on the silica microstructure.

Wei et al. (2008) reported the use of a (trifluoropropyl) triethoxysilane (TFPTES) to make a hydrophobic silica membrane. The overall H_2 permeance and H_2/CO_2 separation factor almost remained constant even after exposure to water vapor for 220 h, in contrast to the pure silica membranes. Castricum et al. (2008) reported a membrane with very small pores from organically bridged silanes prepared from mixing bis(triethoxysilyl)ethane (BTESE) and MTES. Their membranes exhibited a very slow decrease in permeance that remained stable and was highly selective after almost 2 years of continuous operation at 150°C for alcohol dehydration. Kanezashi et al. (2010) used BTESE to shift the silica networks to a larger pore size for an increase in H_2 permeability while the membranes also reached high H_2/SF_6 selectivity and showed high hydrothermal stability. Qi et al. (2011) used BTESE to modify silica networks by adding niobium. The membrane exhibited excellent H_2/CO_2 separation performances and high enough hydrothermal stability. Ahn et al. (2018) created a silica membrane for hydrogen separation with a precursor vinyltriethoxysilane (VTES) with alumina support using CVD method at 600°C. This membrane showed a high permeance value of hydrogen, up to 5.4×10^{-7} mol m^{-2} s^{-1} Pa^{-1}; hydrogen selectivity to CO_2, N_2, CO, and CH_4 were 95, 170, 170, and 480, respectively. In a test with water vapor exposure of 16 mol% at 600°C for 72 h, VTES membrane had higher hydrothermal stability than a silica membrane made from pure TEOS. Yamamoto et al. (2018) used a dioxane-bridged (BTES-ED) alkoxysilane containing 1,4-dioxane moieties as a bridged silica membrane precursor. The resulting membrane works well as a gas membrane with selective permeation properties (H_2/SF_6 = c.1900). Also, this membrane can be used as a reverse osmosis membrane with 98.5% salt rejection and desalination performance of 1.84×10^{-13} m^3 m^{-2} s^{-1} Pa^{-1}.

In addition to using an alkyl group binding to Si, some researchers used Si-halides such as Si-F to produce a more stable silica network, which is known as a pendant-type alkoxysilane (Kanezashi et al., 2018). One pendant-type alkoxysilane containing Si-F bonds is triethoxyfluorosilane (TEFS). Some researchers explain that TEFS decreased Si—OH density (Shibata et al., 1988; Maehana et al., 2011; Chiodini et al., 2012). Also, the use of Si—F groups could control the hydrophobic/hydrophilic properties of the resulting silica; it even affected the siloxane bond angles (Kanezashi et al., 2017). Therein, Kanezashi et al. (2017) prepared the membrane using TEFS as a silica precursor. This membrane displayed high permeance of hydrogen (2.0×10^{-6} mol m^{-2} s^{-1} Pa^{-1}) and high hydrogen selectivity compared to SF_6 molecules (H_2/SF6 > 18,000). Evaluation of hydrothermal stability was performed by measuring the permeance of each gas in the presence of water vapors (at a partial pressure of vapor 30 kPa and a temperature of 300°C). The TEFS membrane demonstrated a decrease in the value smaller than the TEOS-derived membrane. This result concluded that Si-F improved the hydrothermal stability of the silica structure (Kanezashi et al., 2018).

Qi et al. (2012) reported the fabrication of hybrid silica membranes using BTESE doped by Nb. The results showed that the permeability of H_2 reached 6.28×10^{-8} mol m^{-2} s^{-1} Pa^{-1}, and the permselectivity of H_2/CO_2 was 108 with acceptable stability in hydrothermal treatment. However, other studies have shown that the use of palladium as dope for organosilica membranes produced better organosilica membranes in permeability and thermal stability compared with a Nb-doped membrane (Song et al., 2016). At the separation of hydrogen gas, the addition of Pd increased the permeability of H_2 and gas separation capabilities (Kanezashi et al., 2013; Boon et al., 2015; Li et al., 2016; Naga Mahesh et al., 2016). The Pd-doped organosilica (POS) membrane calcined in steam atmosphere exhibited good hydrogen separation performance (H_2 permeance 2.5×10^{-7} mol·m^{-2}·s^{-1}·Pa^{-1}) (Lei et al., 2017).

A second strategy deployed to functionalize silica membranes was the carbonization of surfactant templates in the silica matrix. This was achieved by preparing a functional carbonized-template molecular sieve silica (CTMSS) using a novel surfactant templating procedure. Duke et al. (2004, 2006) developed CTMSS membranes to improve hydrostability of a silica matrix without decreasing initial selectivity. Their method involved the carbonization of surfactants embedded in silica matrices at high temperatures and under vacuum or nonoxidizing atmospheres. It was found that selectivity improved over conventional silica membranes while maintaining high hydrothermal stability.

The third strategy, which became quite attractive since 2005, is to incorporate metal oxides or metal into silica membranes. Inorganic oxides such as Al_2O_3 (Fotou et al., 1995; Gu et al., 2008), NiO (Kanezashi et al., 2005; Kanezashi and Asaeda, 2006, 2005; Xomeritakis et al., 2009), CoO (Uhlmann et al., 2009, 2010, 2011; Battersby et al., 2009a, b; Smart et al., 2012; Brands et al., 2010), B_2O_3 (Barboiu et al., 2009), TiO_2 (Gu and Oyama, 2009; Farhang-Ghoje Biglu and Taheri-Nassaj, 2013), ZrO_2 (Araki et al., 2011; Choi et al., 2013; Tsuru et al., 1998), Nb_2O_5 (Qi et al., 2011, 2012), and Ag (Yang and Chen, 2013) have been used to improve the performance of silica membranes. Although early attempts before 2005 resulted in membranes with low gas separation performance, it was found that metal oxides significantly increase the hydrothermal stability of metal oxide-doped membranes. Gu et al. (2008) reported that a composite silica-alumina membrane had high permeability for hydrogen in the order of 10^{-7} mol m^{-2} s^{-1} Pa^{-1} at 500°C with a selectivity of H_2 over CH_4, CO, and CO_2 of 940, 700, and 590, respectively, and exhibited much higher stability to water vapor at the high temperature of 873 K in comparison to pure silica membranes. Smart et al. (2012) reported that cobalt oxide silica membranes had H_2 permeance of 1.9×10^{-7} mol $m^{-2}s^{-1}Pa^{-1}$ in conjunction with an H_2/CO_2 permselectivity of more than 1500. These membranes had the high thermal stability to resist thermally induced densification up to at least 600°C. Nickel oxide was also shown to provide stability against silica densification caused by SO_2 exposure (Xomeritakis et al., 2009). Uhlmann et al. (2011) prepared cobalt oxide membranes xerogels exposed to H_2S, H_2O, and $H_2S + H_2O$ at varying H_2S concentrations and times at 200°C for a total of 150 h and found H_2S had no significant chemical or structural change upon exposure. Yacou et al. (2012) reported that molecular sieve silica membranes doped with cobalt oxide were thermally stable for dry gas separation up to 500°C for 2000 h operation. This work also reported the scale up to a multitube module containing eight membranes in four parallel lines with a total area of 545 cm^2.

Until 2015, metal doping on silica focused on the use of single metal nanoparticles into the silica matrix. Cobalt is the most widely studied dopant because it provides the best results. For the first time, integrated the silica membrane with cobalt palladium binary metal nanoparticles was prepared by Ballinger et al. (2014). There was a selective reduction in which, by exposing membrane to hydrogen at 500°C, the cobalt remained in the oxide form yet the palladium was reduced to the metal. This then produced a molecular gap that resulted in a different performance when the membrane was oxidized and reduced. Ballinger et al. (Ballinger et al., 2015) also prepared a silica membrane embedded in a cobalt lanthanum binary metal. A permeation test was conducted for 350 h in which carbon dioxide was used and the membrane was reduced. There was an increase in H_2/CO_2 permselectivity indicating the presence of large pore closures, making it advantageous for increased selectivity. This result differs from the general view where there is a small pore closure and thermal densification in the permeation process. Darmawan et al. (2015) reported on the synthesis of iron/cobalt oxide silica membranes. It was found that a high amount of iron produced a membrane containing larger pores resulting in a low He/N_2 permselectivity value; on the other hand, high cobalt composition produced a higher He/N_2 permselectivity.

Igi et al. (2008) explained how metal doping improves hydrothermal stability. It was concluded that the metal oxides doped in silica could prevent the introduction of H_2O and resist the reaction of the Si—OH group. The metal nanoparticles in the silica matrix have been shown to affect the performance of the silica membranes in which the metal oxide forms increased hydrothermal stability (Kanezashi and Asaeda, 2005; Uhlmann et al., 2009), whereas the nonoxidized metals produced selective adsorption and hydrogen permeation (Ikuhara et al., 2007).

The fourth strategy is by preparing an alumina-silica composite. Kageyama et al. (2018) synthesized a silica-alumina composite membrane using γ-alumina as membrane support. They reacted aluminum tri-sec-butoxide with tetraethylorthosilicate the through CVD method. Compared with the silica membrane, the silica-alumina composite membrane exhibited higher hydrothermal stability. This membrane displayed stability in hydrothermal treatment over 60 h with a content of 16 mol% H_2O at 650°C.

Another parameter that can be used to improve thermal stability is by optimizing the thermal treatment conditions. The temperature of calcination, time, and atmospheric conditions significantly influenced the structure of the silica membrane. Kanezashi and Asaeda (2006) showed that hydrothermal treatment of the membrane at a pressure of 90 kPa at 650°C before the membrane was used to separate H_2 was effective in preventing densification compared to a membrane not previously stored in the vapor. Moreover, Ryosuke et al. (2008) reported the synthesis of a 33 mol% Co-doped on silica membrane, which indicated that the best permeation performance of H_2 was obtained under the conditions of the vapor atmosphere (600°C, vapor pressure of 90 kPa). The silica membrane showed stable gas permeance and an H_2 permeate of about 2.00–4.00 × 10^{-6} mol s^{-1} m^{-2} Pa^{-1} with selectivity 250–730 (H_2/N_2) even up to 60 h exposure of steam.

Recent developments have shown that silica membranes can be prepared on the supports without mesoporous interlayers. Liu et al. (2015) for the first time prepared silica membranes without using interlayers in which the α-alumina macropore substrate was coated directly with a thin film of silica. They used amorphous silica seeds bonded to the polymeric sol and produced a tissue blocking the silica infiltration on the alumina support, hence it was strong enough to avoid cracking. The silica seed was prepared using the Stöber method whereas the cobalt silica sol was synthesized through the sol-gel processes. Then, the silica seeds and cobalt silica sol were mixed and deposited on an alumina support. Silica seeds could support silica polymers and soften pores on an alumina support. This membrane produces hydrogen permeance of 2.6×10^{-7} mol m^{-2} s^{-1} Pa^{-1} and He/N_2 selectivity of 97 at 500°C.

5.2 Silica Membrane for Desalination

For desalination applications, the silica membrane pore size is controlled to allow the water molecules to diffuse, though hydrated salt ions can be retained. A water molecule has a kinetic diameter (0.26 nm) whereas hydrated salt ions are larger. Na^+ and Cl^- are 0.72 nm and 0.66 nm, respectively (Lin et al., 2012; Han and Peng, 2016). Therefore, the arrangement of the membrane structure of silica becomes important to obtain high salt rejection. Like the application on gas separation, the main problem of using silica membranes for desalination is related to the instability of the silica matrix when exposed to water. This relates to the hydrophilic nature of silanol (Si—OH). The interaction between water and siloxane bonds (Si—O—Si) causes hydrolysis of siloxane (Si—O—Si) bonds and forms mobile silica phase (Duke et al., 2006). The latter will cause the pore dilution within the silica matrix leading to a formation of defects, which automatically reduces the separation performance (Giessler et al., 2003).

Similar to the effort to solve the problem of gas separation, several attempts were made. For more than 2 decades there have been attempts to improve silica membrane hydrostability. The efforts included introducing an organic template into the silica matrix (Raman and Brinker, 1995; Giessler et al., 2001). The presence of a hydrophobic carbon group protects the silica group to be hydrolyzed. Hence micropore structure damage can be inhibited. In the desalination application with a 3.5% NaCl feed solution, the carbonized silica membrane can reject salt up to 96% with water flux reaching 2 kg m^{-2} h^{-1} (Duke et al., 2007). Elma et al. (2015a) investigated the use of Pluronic® P123 triblock copolymer added to the silica membrane. The flawless membrane was yielded by vacuum calcination. Hence this membrane demonstrated an excellent salt rejection (>99.5%). It was found that the high content of organic groups significantly reduced the polarization of salt concentrations. Micropore and mesoporous structures combined to provide molecular sieving properties, yet producing large pore volumes that implied a high water flux. Organic silica precursors containing nonhydrophilic carbon-carbon bridges between silicon atoms called *periodic mesoporous organosilica* (PMO) are used to increase the membrane strength (Chua et al., 2015b). Thereby, reduction of the hydrolysis process on the silica matrix has been achieved (Xu et al., 2011; Chua et al., 2013). In PMO, organosilica scaffolds bind covalently to organic groups and are uniformly distributed in the silica matrix (Dag et al., 2001; Park and Ha, 2004). A silica membrane using a silica precursor of dioxane-bridged alkoxysilane, 2,5-bis [2-(triethoxysilyl) ethyl]-1,4-dioxane was prepared and used in a reverse osmosis process (Yamamoto et al., 2018). The membrane showed a reverse osmosis separation with a permeability of 1.84×10^{-13} m^3 m^{-2} s^{-1} Pa^{-1} and a rejection of NaCl of 98.5%. Although the water flux is lower than the commercial polyamide membrane, this membrane showed better thermal stability. Chua et al. (2013) prepared a membrane with an excessive desalination performance with a water flux of up to 13 kg m^{-2} h^{-1} at extreme salt concentrations up to 15 %wt using the organosilica precursor. No polarization concentration was observed with increasing salt concentration, but the temperature polarization had a significant effect (Chua et al., 2015c).

Further development for desalination applications is by doping metal oxides on the silica matrix. Lin et al. (2012) for the first time synthesized cobalt oxide silica membranes for desalination and found that the silica membrane was stable and showed good performance for desalination testing over 575 h. The highest saline rejection reaches over 99% and can separate the feed with a very salty concentration (7.5–15 wt% NaCl). Further Elma et al. (2015b) prepared the cobalt oxide silica directly coated on the macropore alumina support. These membranes exhibited a high salt rejection performance (up to 99%) for salt concentrations of up to 7.5%. The membrane model without an interlayer is attractive as it reduces the preparation time significantly but still produces a quality membrane. Darmawan et al. (2016)) reported the use of nickel oxide/silica membrane in desalination with a rejection rate as high as 99.8%. The same study reported that the highest flux can be observed for the membranes made with Ni/Si molar ratio of 25%. Meanwhile, the addition of H_2O_2 catalysts results in a denser structure subsequently leading to higher salt rejection.

The use of pendant-type alkoxysilane was applied in the preparation of silica membranes for desalination. Yang et al. (2017a) reacted the vinyl group containing triethoxyvinylsilane (TEVS) as pendant-type silica with a Pluronic triblock copolymer (P123) template. This membrane demonstrated a water flux of 26.5 L m^{-2} h^{-1} (NaCl 1% and operating temperature 60°C) with a 99.5% salt rejection.

5.3 Silica Membrane in Ammonia Separation

Subsequent development in silica membrane applications is their use for ammonia separation. The difference in diameter of water molecules (0.26 nm) and larger ammonia molecules (kinetic diameter 0.326 nm (van Leeuwen, 1994)) theoretically allows water to be separated from ammonia. On the other hand, if ammonia entered the pore of the silica membrane, there was a strong interaction between silica and ammonia, which competed with the interaction between silica and water. This can cause rapid degradation of the silica membrane. Therefore, as for gas separation and desalination applications, it is necessary to improve the stability of the silica membrane. Previous reports have suggested that the silica membrane is damaged with excess acid feed but not many reports relate its application to basic conditions. Few studies have reported the separation of ammonia from aqueous solutions by pervaporation (PV)

(Yang et al., 2014, 2016). Yang et al. (2014) found that iron-doped membrane silica shows the highest permeate flux, however, it had a low ammonia selectivity.

On the other hand, the cobalt-doped silica membrane exhibited excellent selectivity against ammonia; nevertheless, this membrane quickly experienced degradation in a short span of time. The cobalt-doped silica membrane could concentrate ammonia up to 12 times from initial concentration and had a high selectivity of ammonia up to 60 times. It also reported the use of silica membranes to reduce ammonia levels from industrial waste (Yang et al., 2017b).

6 Conclusions and Future Trends

Research interest into silica membranes, their synthesis techniques, analysis methods, and potential applications remains at an all-time high despite being an active field of research for almost 30 years. RTP leading to a fast fabrication of silica membranes is one of the major achievements in recent years. The other positive outcomes are the increase of the hydrothermal stability in the case of the metal oxide/silica and hybrid silica. However, the latter achievement is not yet sufficient for the membrane application in the presence of water and water vapors. Thus, the membrane hydrothermal stability remains a major challenge and an application limiting factor. Yet, significant advances have to be made before the silica membranes can be applied in the industrial processes operating in presence of water or water vapors, especially at elevated temperatures.

List of Acronyms

BTESE	bis(triethoxysilyl)ethane
CVD	chemical vapor deposition
ES40	ethyl silicate 40
FTIR	Fourier transform infrared
IEP	isoelectric point
MTES	methyl triethoxy silane
Pluronic® P123	triblock copolymer poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide)
PMO	periodic mesoporous organosilica
PV	pervaporation
RTP	rapid thermal processing
SEM	scanning electron microscopy
SR	steam reforming
TEFS	triethoxyfluorosilane
TEOS	tetraethyl orthosilicate
TEVS	triethoxyvinylsilane
WGS	water gas shift
XPS	X-ray photoelectron spectroscopy

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