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Various fabrication methods of porous ceramic supports for membrane applications

Abstract: In this article, a general review on porous ceramic membrane supports was done with reference to fabrication methods. Each method was detailed, along with the raw materials used for the fabrication of membrane supports. Characteristics such as pore size and porosity of the porous membrane support were summarized for each fabrication method from the viewpoint of sintering temperature, starting raw materials, sintering aids, and additives. Membrane supports fabricated by various fabrication methods such as powder pressing, colloidal processing, and paste processing were reviewed. This will be helpful for beginners in selecting a suitable fabrication method to shape their membrane and utilize the membrane support for further processing such as selective layer formation, which plays an important role in separation performance.

Keywords: colloidal processing; membrane support; paste processing; powder processing.

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1 Introduction

Fabrication of ceramic membranes for new processes and new applications has undergone rapid growth during the last three decades. The rapidly changing environmental legislation in the use of chemicals and reagents also makes them very attractive. Performance in terms of permeability of ceramic membranes mainly depends on the porous membrane support. Fabrication of suitable ceramic support for membrane application has been a challenging task for the researchers. Few researchers

used the support (without skin/selective layer and the average pore size are in the micrometer range) itself as a microfiltration membrane. Usually, supports with average pore diameters >1 mm are not considered as membrane supports, and they must be considered as macroparticle filters. Many steps have been involved in the fabrication of ceramic support. The major factors that must be considered during the fabrication of ceramic supports are properties of the starting raw materials/precursors, method of preparation of the powder/paste, method of fabrication, and sintering/heat treatment method.

Normally, the starting raw materials used for the support fabrication decides the sintering temperature, pore characteristics (porosity, pore size, and tortuosity), and cost (economy) of the membrane (Burggraaf and Cot 1996). Raw materials are prepared in a powder, paste, or colloid form that suits the fabrication methodology. The method of fabrication decides the geometry of the final product. Flat-, circular-, or tubular-shaped membrane supports are fabricated in laboratories and experimented for their performance. Furthermore, complicated fabrication methods have been used for the preparation of monoliths (honeycomb) and hollow-fiber modules for industrial application to process large volumes of feed (Burggraaf and Cot 1996). A proper ceramic support should possess good permeability, mechanical strength, narrow pore-size distribution, and specific surface area. Huge volumes of reports were found for membrane supports fabricated using high-purity α -alumina. In recent years, many efforts have been made to prepare mullite ceramics to reduce fabrication cost. Mullite ceramics have been synthesized from various inexpensive natural materials such as kaolin, bauxite, cordierite, diatomite, andalusite, and sapphire (Palacio et al. 1998, Bouzerara et al. 2006, Dong et al. 2008, Akhtar et al. 2010, Bejjauoui et al. 2010, Dong et al. 2010, Esharghawi et al. 2010). Although many reviews on selective layers have been reported in the open literature, there are not many reviews on the fabrication methods of supports for membrane applications. In view of this, the present review focused on the classification of porous membrane supports based on the fabrication methods. This will be very helpful for new researchers in fabricating membrane supports for membrane applications.

2 Ceramic support fabrication

Researchers use various ceramic support fabrication methods. Most membrane supports (commercial and homemade) are fabricated by powder pressing, paste processing, and colloidal processing methods. A detailed classification is shown in Figure 1.

2.1 Powder pressing method

The powder pressing method has been used for the preparation of ceramic tiles and high-density products in the earlier stages. Later on, because of the characteristics of the ceramic materials, there were attempts to use this method for the fabrication of membrane supports.

Typically, two types of pressing methods, axial pressing and isostatic pressing, have been used for the fabrication of membrane supports. The axial pressing (uniaxial and biaxial) method is inexpensive and suitable for high-volume production of simple geometrical shapes such as flat and circular supports. Axial pressing is classified into two types, namely, dry pressing and wet pressing. Wet pressing involves the addition of fluid, especially water, to the ceramic raw materials for shaping, and dry pressing involves only the dry powders without addition of water.

In isostatic pressing, pressure is applied from multiple directions to achieve greater uniformity of compaction and increase shape capability compared with uniaxial pressing. Isostatic pressing methods are classified into cold and hot isostatic pressing. In cold isostatic pressing (CIP), the isostatic pressure is created by applying external pressure onto the fluid, normally water or oil. This pressure is uniformly applied to ceramic powder to form

the required shape of the membrane support. In the case of hot isostatic pressing, the isostatic pressure is created by heating the encapsulated fluid (mostly argon gas) to the working temperature. This isostatic pressure forms the ceramic support of desired shape.

Many circular-shaped membrane supports were fabricated using high-purity α -alumina of various particle sizes in a mechanical press at high pressures without additives (Jayaraman et al. 1995, Kim and Lin 1999). Over the years, the dry pressing method has been replaced with the wet pressing method by the addition of binders, especially organic binders such as polyvinyl alcohol (PVA), polyacrylic acid (PAA), polyethylene glycol (PEG), and methylcellulose. This increases the green strength (handling strength) and pore network properties of the support (Palacio et al. 1998, Vercauteren et al. 1998, Falamaki et al. 2004a,b, Chang et al. 2005, Wang et al. 2006, Dong et al. 2008). The binder is chosen in such a way that it must be completely burned off during sintering without leaving any ashes on the membrane support. The pore growth in the membrane support is a function of the initial powder particle size and compaction pressure (Falamaki et al. 2004a). The investigation focused on the evolution of typical membrane characteristics, such as permeability and tortuosity, of α -alumina and zircon ($ZrSiO_4$) membrane supports, and it revealed that the porosity, shrinkage, and mean pore size mainly depend on the sintering temperature (Falamaki et al. 2004a). Enhancing the particle size of the raw materials increases the pore size of the membrane along with the compaction pressure (Kim and Lin 1999, Falamaki et al. 2004a,b). Only a significant change has been observed in the porosity of the membrane supports with an increase in the sintering temperature. However, it is greatly decreased with increased compaction pressure and decreased raw material particle size (DeVos and Verweij 1998, Kim and Lin 1999, Chang et al. 2005, Wang et al. 2006, Dong et al. 2008). However, there is a limitation for compaction pressure and particle size of the raw materials. Increased sintering temperature results in the densification of the support, which always decreases the permeability and increases the mechanical strength of the support. Most research concluded that the optimum sintering temperature of a membrane support is the temperature when the membrane support possesses maximum permeability along with a reasonable mechanical strength (DeVos and Verweij 1998, Falamaki et al. 2004a, Bouzerara et al. 2006, Wang et al. 2006).

Few works have been reported on the fabrication of membrane supports by isostatic pressing method (Luyten et al. 1997, DeVos and Verweij 1998, Vercauteren et al. 1998, Gu et al. 2003, Fukushima et al. 2009). Sometimes,

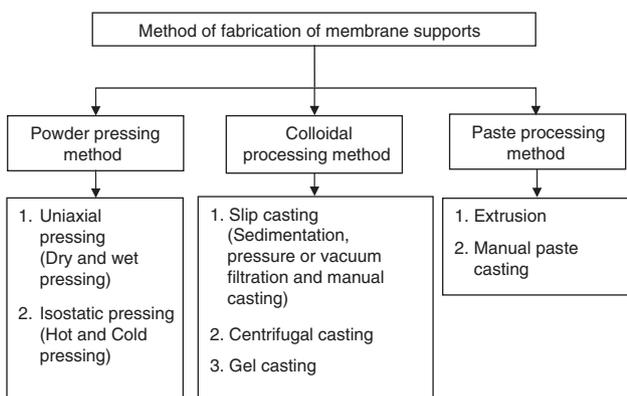


Figure 1 Classification of the membrane supports production methods based on the precursor aggregate state.

support is fabricated by uniaxial pressing followed by isostatic pressing (Luyten et al. 1997, DeVos and Verweij 1998). These investigations revealed that the isostatic pressing results in dense membrane supports with higher mechanical strength than uniaxial pressing. Tubular-shaped membrane supports could also be fabricated by isostatic pressing methods (Luyten et al. 1997, DeVos and Verweij 1998).

Typically, most of the membrane supports are fabricated with high-purity α -alumina powder as starting material and sintered at a high temperature, which increases the cost of the membranes (Luyten et al. 1997, DeVos and Verweij 1998, Dong and Lin 1998, Vercauteren et al. 1998, Kim and Lin 1999, Falamaki et al. 2004a,b, Wang et al. 2006). The typical sintering temperature of alumina, titania, and zirconia membrane supports inevitably increases the production cost. Many research works have been focused to reduce the sintering temperature (Zeng and Gao 1999, Chakradhar et al. 2006, Wang et al. 2006, Dong et al. 2008). Zeng and Gao (1999) pointed out that the reduced particle size of α - Al_2O_3 (<20 nm) resulted in a low sintering temperature (<1000°C). Several low-temperature sintering strategies (such as liquid phase-assisted sintering) have been followed, which involves doping of transition metal oxide and high reactivity nanometric-size powders with support raw materials (Luyten et al. 1997, Zeng et al. 1998, Sathiyakumar and Gnanam 2002, Wang et al. 2006, Dong et al. 2008, Fukushima et al. 2009). Organic binders are replaced with inorganic sintering aids, which have been used to decrease the sintering temperature and enhance the pore property, porosity, and strength of the membrane support. Among the inorganic sintering aids, calcium carbonate is widely used to increase the porosity of the membrane support. Other carbonates such as magnesium carbonate, sodium carbonate, and calcium magnesium carbonate have also been used as porosifiers (Palacio et al. 1998, Bouzerara et al. 2006, Fukushima et al. 2009). The decomposition of CaCO_3 produces the largest pores at lower temperature (<1000°C). However, a higher temperature (>1300°C) leads to reduced pore size due to the liquid phase sintering mechanism, which produces low-melting calcium-aluminate and calcium-aluminate-silicate species (Falamaki et al. 2004b). In addition, it also reduces the tortuosity and roughness of the membrane support, which results in more rounded pores. Their work confirmed that with proper process parameters (such as sintering temperature and amount of porosifier), it is possible to fabricate rounded pore membrane supports with higher permeability. Wang et al. (2006) fabricated ceramic supports using α -alumina with titania (rutile) as sintering aid, and their observations revealed that the addition of

rutile powder to alumina drastically reduces the porosity, pore size, and the corrosion resistance of the membrane support.

Addition of organic additives such as PVA, PEG, PAA, etc. only has a significant effect (no significant changes in pore size after the binder removal) on pore size. Furthermore, the addition of inorganic additives/sintering aids such as CaCO_3 , titania, silica, and cordierite leads to unimodal or multimodal pore size distribution based on the chosen particle sizes. When the difference between the particle size of the starting raw material and inorganic additives are high, a wider pore size distribution occurs, which decreases the selectivity of the membrane support. Moreover, nonuniform pore size distribution affects the selective layer coating on the support and has high tendency to form cracks.

Several research works have been focused on other ways of reducing the cost of the ceramic support by using locally available low cost raw materials (Palacio et al. 1998, Bouzerara et al. 2006, Dong et al. 2008). To reduce the fabrication cost, mullite-based ceramic supports have been synthesized from various inexpensive natural materials/clays such as kaolin, bentonite, and smectite. Kaolin-based mullite ceramic supports have been found to be one of the best alternate for α -alumina, due to its outstanding properties, such as low thermal conductivity and expansion, excellent creep resistance, and excellent thermal, chemical, and mechanical stability. In addition, it retains porosity at elevated temperatures. To increase the concentration of the mullite phase, similar types of raw materials/clays are added with the starting raw material (Palacio et al. 1998, Bouzerara et al. 2006, Chakradhar et al. 2006, Dong et al. 2008, Bi et al. 2011, Monash and Pugazhenthii 2011a,b). The addition of wollastonite to the ceramic mixtures reduces the sintering time and temperature and increases the strength of the membrane supports (Chakradhar et al. 2006, Bi et al. 2011). Increased pressure leads to an increase in the green support strength as well as reduction in pore size (Falamaki et al. 2004a,b). However, there will always be an optimum pressure, beyond which the pressing pressure has no significant effect. In addition, the pressing pressure is based on the particle size of the raw materials. Sometimes, high pressure leads to difficulty in removing the green supports from the molds or die, and high pressure also leads to imperfections (mild cracks) in the ceramic membrane support. An increase in sintering temperature leads to an increase in pore size and, to certain a extent, porosity. If the sintering temperature is increased beyond the optimum temperature (must be experimented for each material based on the other set parameters), both pore

size and porosity tend to decrease due to the densification of the support. More dead ends of the pores resulted in low permeability and not suitable for membrane support. Normally, mechanical strength increases with increasing pressing pressure and sintering temperature. A starting material with smaller particle size has higher mechanical strength than a raw material with a large particle size. The tensile/mechanical strength of the membrane supports are usually determined by diametral compression test, three- and four-point bending tests. The mechanical strength of the supports fabricated by powder pressing method is presented in Table 1. However, the mechanical strength of the membrane supports is varied based on the testing methods and testing conditions such as specimen size, span width, and cross-head speed of the testing machine. Thus, the testing method and details of the testing specimen and conditions are also provided in Table 1 for homogeneity and comparison. Typically, α -alumina or silica particles of smaller size (with narrow particle size distribution) and high sintering temperature give high strength to the ceramic membrane support compared with that of other supports discussed in literature. The probability of bending of the green support during sintering is lower compared with that of other processing methods, especially colloidal and paste processing, due to the minimal amount of water used in the fabrication of the membrane support. However, the support must be sintered at a controlled heating rate (preferably low heating rate, depending on the support raw materials) to avoid thermal shock waves that lead to bending of the support during sintering. Thus, the support size and thickness (it indirectly fixes the pressing pressure) are fixed; the variables that affects the characteristics of the supports are particle size distribution and average particle size of the raw materials (also covers sintering aids) and sintering temperature. Normally, the average pore size of the membrane supports prepared by pressing method ranges between 0.1 and 1 μm (Vercauteren et al. 1998, Kim and Lin 1999, Falamaki et al. 2004a, Wang et al. 2006, Fukushima et al. 2009). Membrane supports fabricated by powder pressing method are presented in Table 1.

2.2 Colloidal processing method

The term “colloid” is used to describe particles that possess at least one dimension in the size range 10^{-3} to 1 μm . A distinguishing feature of all colloidal systems is that the contact area between particles and the dispersing medium is large. As a result, interparticle (or surface) forces strongly influence suspension behavior. In general, colloidal processing

involves a sequence of steps such as powder synthesis and purification (if commercial powder is used, then the synthesis step is not required, and only purification may be required), colloidal/suspension preparation, consolidation into the desired component shape, removal of the solvent phase, and heat treatment (sintering temperature) to produce the membrane support for optimal performance. Based on the consolidation mechanism, the colloidal processing methods are classified into three major classifications, namely slip, centrifugal, and gel casting. In slip casting, ceramic membranes have been fabricated by pouring a stable slip (suspension of clay or ceramic material in water) in a porous mold, especially gypsum mold, or in nonporous surfaces, such as Petri dishes or glass plates. Based on the fabrication method and solvent-removal mechanism, slip casting is termed as sedimentation (Darcovich et al. 2001, Wang et al. 2001, Weir et al. 2001), pressure or vacuum filtration (Garrido and Aglietti 2001, Shqau et al. 2006, Maleksaeedi et al. 2008, Mottern et al. 2008), and simply slip casting, which refers to casting the slip in porous molds (Hyun and Kang 1994, Huang and Chen 1995, Erdem et al. 2006). The membrane supports fabricated using colloidal processing methods are listed in Table 2.

The most important and challenging task involved in the fabrication of membrane support by slip casting process is the preparation of stable colloidal suspension. This can be achieved by controlling various interaction forces such as van der Waals, steric, electrostatic, and interparticle forces. The particle size and its concentration in the slip determine the pore characteristics of the membrane supports. It is well known that the pore size distribution of the membrane supports depends on the state of aggregation of the particles, which could be controlled with the addition of surfactants or dispersing agents and acids or bases. Widely stable slips are obtained by controlling the pH at a particular value (Hyun and Kang 1994, Huang and Chen 1995, Darcovich et al. 2001, Erdem et al. 2006). Usually, the colloidal suspensions are in dispersed and flocculated (weakly or strongly flocculated) states.

In practice, ammonium polymethylacrylic acid electrolyte (NH_4^+PMA , commercially known as Darvan C) is used as a dispersing agent (Hyun and Kang 1994, Darcovich et al. 2001, Steenkamp et al. 2002, Erdem et al. 2006) and starch as a pore-forming agent (Erdem et al. 2006), and pH was adjusted with either acids or bases (Darcovich et al. 2001, Chowdhury et al. 2005, Shqau et al. 2006). In addition, PVA is used as a binder as well as a colloid stabilizer (Huang and Chen 1995), and sometimes inorganic ceramic materials such as kaolin, CaCO_3 , SiO_2 , alumina, and yttria are used as sintering aids (Moreno et al. 1999, Xiang et al. 2002).

Table 1 Membrane supports fabricated by powder pressing method.

Support materials	Support details	Sintering details	Additives	Pore Size	Total porosity	Bending strength	Reference
Diatomite powder (mean particle size=12.79 μm) Kaolin (mean particle size=1.53 μm) Prepared by dry pressing method	Circular disk support: Diameter=40 mm Thickness=4 mm Pressed at 18.7 MPa	Sintering temperature: 900°C–1200°C Soaking time: 1 h	PEG as binder	0.4–1.2 μm	–	56 MPa Three-point bending test	Ha et al. 2013
Fly ash Bauxite powder (mean particle size of the mixture=15 μm) Prepared by uniaxial pressing method	Circular disk support: Diameter=25 mm Thickness=2–3 mm Pressed at 160 MPa	Sintering temperature: 1300°C–1500°C Heating rate: 1°C/min up to 450°C and 2°C/min for 1500°C Soaking time: 2 h	Titania PVA as binder	6.5–7.6 μm	42–46 vol%	28–36 MPa Three-point bending test Test specimen size: 40×5.92×3.2 mm (bar type) Span length: 30 mm Cross-head speed: 0.5 mm/min	Dong et al. 2011
Diatomite powder Prepared by uniaxial pressing method	Momolith support: Diameter=10 mm Pressed at 50 MPa	Sintering temperature: 900°C–1400°C Heating rate: 5°C/min Soaking time: no soaking time	PEG as binder	0.2 μm	>50 vol%	106 MPa Diametral compression test Cross-head speed: 0.5 mm/min	Akhtar et al. 2010
Andalusite powder (<40 μm) Quartz Dolomite Prepared by dry pressing method	Circular disk support: Diameter=22 mm Pressed at 6 MPa for 10 min	Sintering temperature: 1150°C–1350°C Heating rate: 10°C/min Soaking time: 2 h	No binder	10–120 μm	–	–	Beijaoui et al. 2010
Kaolin Quartz Calcium carbonate (the particle size of the mixture is <5–30 μm) Prepared by uniaxial pressing method	Circular disk support: Diameter=62 mm Thickness=5 mm Pressed at 50 MPa	Sintering temperature: 900°C–1000°C Heating rate: 2°C/min Soaking time: 6 h	PVA as binder	1.30 μm	30 vol%	46 MPa Three-point bending test Test specimen size: 55×5×5 mm (bar type) Span length: 50 mm Cross-head speed: 0.5 mm/min	Vasanth et al. 2011
Quartz (particle size of the mixture is <1 mm) Prepared by uniaxial pressing method	Circular disk support: Diameter=30 mm Thickness=4 mm Pressed at 10 MPa	Sintering temperature: 1100°C Heating rate: 5°C/min Cooling rate: 5°C/min Soaking time: 1 h	Zeolite Frit glass Water	4–12 μm	38 vol%	–	Ozgur and San 2011

(Table 1 Continued)

Support materials	Support details	Sintering details	Additives	Pore Size	Total porosity	Bending strength	Reference
Kaolin Ball clay Quartz Calcium carbonate Feldspar Pyrophyllite (Particle size of the mixture is ranging between 5 and 10 μm) Prepared by uniaxial pressing method	Circular disk support: Diameter=42 mm Thickness=4 mm Pressed at 50 MPa	Sintering temperature: 850°C–1000°C Heating rate: 2°C/min Cooling rate: 2°C/min Soaking time: 6 h	PVA as binder	1.01 μm	44 vol%	28 MPa Three-point bending test Test specimen size: 60×5×5 mm (bar type) Span length: 50 mm Cross-head speed: 0.5 mm/min	Monash and Pugazhenthi 2011a
Kaolin Prepared by isostatic pressing method	Circular disk support: Pressed at 200 MPa	Sintering temperature: 1500°C–1800°C Heating rate: 5°C/min up to 1000°C and 10°C/min up to 1550°C Soaking time: 5 h	Aluminum powder (<45 μm) Magnesium oxide (<250 μm)	–	56 vol%	–	Esharghawi et al. 2010
Kaolin Prepared by uniaxial pressing method	Circular disk support: Pressed at 200 MPa	Sintering temperature: 1500°C–1800°C Heating rate: 5°C/min up to 1000°C and 10°C/min up to 1550°C Soaking time: 5 h	Aluminum powder (<45 μm) Magnesium oxide (<250 μm)	–	48 vol%	–	Esharghawi et al. 2010
Silicon carbide powder (mean particle size=0.30 μm) Prepared by CIP	Circular disk support: Diameter=20 mm Thickness=5 mm Pressed at 100 MPa	Sintering temperature: 1500°C–1800°C Heating rate: 20°C/min Cooling rate: 1 5°C/min Soaking time: 2 h	α -Alumina and yttria as additives	0.1–0.7 μm	42 vol%	57 MPa Diametral compression test Cross-head speed: 0.5 mm/min	Fukushima et al. 2009
Bauxite Mullite (mean particle size=3.37 μm) Prepared by uniaxial pressing method	Circular disk support: Diameter=15 mm Thickness=2–3 mm Pressed at 200 MPa	Sintering temperature: 1400°C–1600°C Heating rate: 1°C–3°C/min Soaking time: 0.5 h	PVA-1750 (5.7 wt%) as binder	–	6 vol%	70.85 MPa (1400°C) and 186.19 MPa (1600°C) Three-point bending test Test specimen size: 50×6×4 mm (bar type) Span length: 30 mm Cross-head speed: 0.5 mm/min	Dong et al. 2008

(Table 1 Continued)

Support materials	Support details	Sintering details	Additives	Pore Size	Total porosity	Bending strength	Reference
α -Alumina and titania (median particle diameter=0.43 μm) Prepared by uniaxial pressing method	Circular disk Diameter=22 mm Thickness=1.5 mm Pressed at 240 MPa	Sintering temperature: 1400°C Heating rate: 4°C/min Soaking time: 2–10 h	Methylcellulose (2 wt%) as binder Corn starch (2 wt%) as pore-forming agent	1.6–0.8 μm	47 vol%	50 MPa Three-point bending test Test specimen size: 60×5×5 mm (bar type)	Wang et al. 2006
Kaolin and Dolomite Prepared by uniaxial and roll pressing method	Flat configuration Pressed at 75 MPa	Sintering temperature: 1000°C–1300°C Heating rate: 4°C/min Soaking time: 1 h	Methylcellulose (4 wt%) as a plasticizer Amijel (4 wt%) as a binder	0.02–7.68 μm	37–56 vol%	16 MPa Diametral compression test Cross-head speed: 0.2 mm/min	Bouzerara et al. 2006
α -Alumina Zirconia Prepared by CIP	Circular disk support: (only for deformation study)	Sintering temperature: 1400°C Heating rate: 1°C/min Soaking time: 2 h	PAA as binder	2.89 μm	40 vol%	–	Chang et al. 2005
α -Alumina (mean particle size 175 μm) Prepared by uniaxial pressing method	Circular disk support: 20 mm Pressed at 61.8 MPa	Sintering temperature: 1325°C, 1350°C, 1375°C, and 1400°C Heating rate: 3°C/min Soaking time: 1 h	PVA (4 ml of a 2 wt% aqueous solution per 100 g dry powder)	0.61–0.74 μm	40 vol%	25 MPa Four-point bending test Test specimen size: 58×14.5×3.8 mm (bar type)	Falamaki et al. 2004a
1. α -Alumina (mean particle size 160 μm) 2. Zirconia powder (mean particle size 1.78 μm) Prepared by uniaxial pressing method	Circular disk support: 20 mm Pressed at 31.2 MPa	Sintering temperature: 1200°C–1500°C Heating rate: 5°C/min Soaking time: 1 h	PVA (4 ml of a 2 wt% aqueous solution per 100 g dry powder)	–0.5 μm	–50 vol%	10–45 MPa Four-point bending test Test specimen size: 58.4×4.7×3.8 mm (bar type)	Falamaki et al. 2004b
Perovskite-related SCFZ powder (mean particle size=8 μm) Prepared by isostatic pressing	Tubular-shaped support: ID=4.1 mm OD=7.7 mm	Sintering temperature: ~1500°C Soaking time: 5 h	–	–	–	–	Gu et al. 2003
α -Alumina powder (A15, mean particle size=1.6 μm) Prepared by pressing method	Circular/disk-shaped support: Diameter=20 mm Thickness=2 mm	Sintering temperature: 1150°C Soaking time: 30 h	–	0.23 μm	–	–	Kim and Lin 1999

(Table 1 Continued)

Support materials	Support details	Sintering details	Additives	Pore Size	Total porosity	Bending strength	Reference
α -Alumina powder (mean particle size 175, 400, and 600 nm) Prepared by uniaxial and isostatic pressing method	Circular disk support: Diameter=39 mm Thickness=2 mm Pressed at 100 MPa (uniaxial) followed by 4 MPa (isostatic)	Sintering temperature: 1250°C Heating rate: 1°C/min (up to 600°C) and 2°C/ min (up to 1250°C) Cooling rate: 5°C/min Soaking time: 3 h	–	0.16 μ m	40 vol%	–	DeVos and Verweij 1998
α -Alumina powder Prepared by uniaxial pressing method	Disk-shaped supports Pressed at 20–30 MPa	Sintering temperature: 1100°C	Organic binder	–	40 vol%	120 MPa Four-point bending test	Vercauteren et al. 1998
α -Alumina powder	Circular disk support: Diameter=20 mm Thickness=2 mm	–	–	0.20 μ m	50 vol%	–	Dong and Lin 1998
Cordierite powder (mean particle diameter=120 μ m) Prepared by pressing method	–	Sintering temperature: 1280°C Heating rate: 4°C/min Soaking time: 2 h	PVA as binder (25% w/w of 12% w/w PVA in aqueous solution)	0.79 μ m	44 vol%	–	Palacio et al. 1998
1. α -Alumina powder 2. Reaction bonded aluminum oxide powder (RBAO) Prepared by uniaxial (UP), CIP, and HIP	Disk support Rectangular support Pellet support Pressed at 50– 200 MPa (UP and CIP) Pressed at 150 MPa (HIP)	For UP and CIP Sintering temperature: 1100°C Heating rate: 4°C/min Soaking time: 2 h For HIP Sintering temperature: 1185°C–1400°C Soaking time: 0.25–2 h	–	0.2 μ m	40 vol%	25 MPa (α -alumina) 100–150 MPa (RBAO) Four-point bending test	Luyten et al. 1997
α -Alumina powder Prepared by Pressing method	Disk-shaped support Thickness=2 mm	–	–	0.2 μ m	–	–	Jayaraman et al. 1995

Various operations such as stirring, grinding (in ball mills), sonicating, and degassing are used by researchers to obtain a homogeneous slip solution (Huang and Chen 1995, Steenkamp et al. 2002, Shqau et al. 2006). The particle size and surface charge of the starting raw material decide the stability of the slip solution. Many investigations reported different particle sizes of high-purity α -alumina, which were achieved by varying the concentrations of the slips (Huang and Chen 1995, Steenkamp et al. 2002, Shqau et al. 2006). This technique is widely used for the fabrication of ultrafiltration (UF) and nanofiltration (NF) membranes. However, few macroporous supports have also been fabricated using the flocculated slips (Huang and Chen 1995, Darcovich et al. 2001, Erdem et al. 2006). Naturally, the narrow particle size results in narrow pore size distribution, which results in higher selectivity. However, the permeation and separation results reported by Darcovich et al. (2001) revealed that a superior performance was obtained from the functionally gradient pore size membrane supports than the narrow pore size dense membrane supports.

Some researchers use the term sedimentation method for slip casting in a porous mold because the phenomenon is sedimentation. Darcovich et al. (2001) fabricated membrane supports (asymmetric microstructures) with the help of polydispersed slurry using sedimentation method. Two different types of α -alumina powders (Ceralox APA-0.2 and Sumitomo AKP-30) were used for the fabrication of supports with functionally gradient structure and more uniform structure. A steric effect was provided by the addition of NH_4^+PMA , and pH was adjusted with HCl solutions. Their investigation revealed that the mean pore diameter of APA-0.2 varies between 53 and 160 nm, with its sintering temperature attributed to the wide range of particle size distribution; however, the narrow particle size distribution of AKP-30 does not have a significant change in the mean pore size (~100 nm). The porosity of both the membrane supports follows the same trend with sintering temperature, and APA-0.2 is found to have a higher porosity (~60%) than AKP-30 (~40%). Although AKP-30 has the narrow pore size distribution, the permeation and the separation tests showed superior performance for the functionally gradient samples (APA-0.2) compared with the uniform samples.

Wang and colleagues (Wang et al. 2001, Weir et al. 2001) investigated the procedures for the preparation of pure sepiolite membranes without any additives. The sepiolite membranes were prepared by dispersing the purified sepiolite powder in distilled water, and the membrane is fabricated by pouring the suspension in 90-mm Petri dishes. The stabilization of the suspension

was achieved by stirring (magnetic stirrer) and ultrasonic agitation. Their results revealed that stirring and sonication did not significantly affect the pore sizes (stirring=25 nm, sonication=23 nm). However, the higher pore density (number of pores per unit area of membrane) obtained for sonication (67 pores/ μm^2) than that obtained by magnetic stirring (27 pores/ μm^2) confirmed that the dispersion of sepiolite clay is better performed by sonification than by magnetic stirring.

Few researchers used filtration (pressure or vacuum) of the slips to form the green support. The green membrane support is formed on a porous filter that is impermeable for the colloidal particles but permeable for the liquid. In general, the filtration method results in dense membrane supports, and the extent of the applied force, resulting in the accumulation of particles, determines the thickness and pore size of the membrane supports (Moreno et al. 1999, Maleksaeedi et al. 2008). The primary slip of low viscosity and good stable dispersion is necessary to avoid bridging among particles, which led to compressible supports (Maleksaeedi et al. 2008). Many research works have been focused on the processing parameters such as the type and concentration of deflocculant, pH adjuster, milling procedure, homogenization time, presence of sintering aids (such as kaolin, bentonite, alumina, yttria), and sintering temperature.

Moreno et al. (1999) fabricated silicon nitride supports using the slip and pressure casting methods and investigated the stability of the membranes as a function of processing parameters. Alumina and yttria were used as sintering aids. The membrane supports were casted in porous stainless steel mold with an internal diameter of 45 mm covered with filter paper by applying different pressures of 1.7, 3.4, 6.8, and 10.2 MPa. The obtained results revealed that the sintering aids lowers the rate of casting, and the green density of the supports by pressure casting are always lower than the slip casting due to the disturbance in the arrangement of particles by the higher formation rate.

Shqau et al. (2006) fabricated disk-shaped $\alpha\text{-Al}_2\text{O}_3$ membrane supports by vacuum filtration over the polysulfone membrane (pore diameter=220 nm). The effect of the dispersant for the stabilization mechanism was investigated using aluminon solution. Two different α -alumina powders (particle size=300 and 600 nm) were used for the preparation of the membrane supports. Their results revealed that addition of aluminon shifted the isoelectric point by two pH units in the acidic direction compared with the suspension of $\alpha\text{-Al}_2\text{O}_3$ without dispersant. Based on this, they found that pH 9.5 is the optimum pH for stable dispersion. The particle size of

Table 2 Membrane supports fabricated by colloidal processing method.

Support materials	Support details	Sintering details	Additives used for sol preparation	Pore size	Total porosity	Bending strength	Reference
ULSA CGO ($\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$) powder (particle median diameter=0.7 μm)	Circular disk support: Thickness=350 μm Prepared by tape casting method	Sintering temperature: 1100°C Heating rate: 0.25°C/min up to 600°C and 1.67°C/ min up to 1100°C Soaking time: 2 h	Graphite powder as pore- forming agent Poly vinyl butyral Poly vinyl pyrrolidone Methyl ethyl ketone ethanol	0.04–12 μm	>40 vol%	–	Kaiser et al. 2013
α -Alumina powder (mean particle size ≤ 10 μm)	Circular disk support: Diameter=39 mm Thickness=2 mm Prepared by pouring in molds	Sintering temperature: 1400°C–1700°C Heating rate: 3°C/min Soaking time: 1 h	PEG (molecular weight=10000) as dispersant agent Corn starch	1.79–4.28 μm	46–64 vol%	48.11 MPa at 1700°C 15.47 MPa at 1700°C Cold crushing strength test	Khattab et al. 2012
BSCF ($\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$) powder (mean particle size ≤ 1.7 μm)	Circular disk support: Diameter=20 mm Prepared by tape casting method	Sintering temperature: 1100°C Heating rate: 3°C/min Soaking time: 3 h	Terpineol (94 wt%) Ethylene cellulose (6 wt%) Corn starch (20 wt%) as pore former	5–25 μm	34 vol%	–	Baumann et al. 2011
α -Alumina powder (particle median diameter=0.7 μm)	Circular disk support: Prepared by pouring the ceramic slips into a cylindrical plastic dies over plaster of Paris blocks	Sintering temperature: 1300°C Heating rate: 10°C/min Soaking time: 2 h	Starch as pore-forming agent Darvan C as dispersing agent	0.2 μm	49 vol%	–	Erdem et al. 2006
α -Alumina powder (mean particle size=1.2 μm)	Circular disk support: Diameter=20 mm Thickness=2 mm Prepared by slip casting	Sintering temperature: 1400°C–1550°C Heating rate: 10°C/min Soaking time: 1 h	Tiron as dispersing agent PVA as binder	0.2–0.3 μm	42–47 vol%	–	Falamaki and Veysizadeh 2006
α -Alumina powder (mean particle size=1.2 μm)	Tubular support: OD=20 mm Centrifugation speed=3000 rpm Centrifugation time=10 min Centrifugation tube=glass tube 20 mm diameter Prepared by centrifugal casting	Sintering temperature: 1400°C–1550°C Heating rate: 10°C/min Soaking time: 1 h	Tiron as dispersing agent PVA as binder	0.24–0.79 μm	47–51 vol%	–	Falamaki and Veysizadeh 2006
α -Alumina powder (AKP30 mean particle size of 0.30 μm)	Circular disk support: Diameter=39 mm Thickness=2 mm Prepared by colloidal filtration	Sintering temperature: 1100°C	Nitric acid as peptizing agent	0.08–0.12 μm	30 vol%	–	Chowdhury et al. 2005
α -Alumina powders (APA-15 and AKP-30 with mean particle size of 0.62 and 0.40 μm , respectively)	Tubular support: ID=12 mm OD=14 mm Length=125 mm Prepared by centrifugal casting (using steel molds)	Sintering temperature: 1200°C Heating and cooling rate: 1°C/min Soaking time: 1 h	Darvan C as dispersant	0.051 μm (AKP-30) 0.1 μm (AKP-15)	40 vol% (AKP-30) 30 vol% (AKP-15)	1600 MPa at 1200°C (AKP-30) 830 MPa at 1200°C (AKP-30) Three-point bending test	Steenkamp et al. 2002

(Table 2 Continued)

Support materials	Support details	Sintering details	Additives used for sol preparation	Pore size	Total porosity	Bending strength	Reference
Kaolinite (12.06 μm) Aluminum hydroxide (6.14 μm)	– Prepared by gel casting	Sintering temperature: 1200°C Soaking time: 5 h	–	0.76–1.31 μm	58–64 vol%	–	Liu et al. 2001
α -Alumina powders (APA-0.2, and AKP-30 with mean particle size of \sim 0.30 μm)	Circular disk support: Diameter=45 mm Thickness=3.3 mm Prepared by sedimentation	Sintering temperature: 1100°C–1300°C	Sedisperse A-12 as dispersing agent	\sim 0.15 μm (AKP-30) \sim 0.092 (APA-0.2)	60 vol% (for AKP-30) 53 vol% (for APA-0.2)	–	Darcovich et al. 2001
Sepiolite clay powder	Circular disk support: Diameter=90 mm Thickness=0.097–0.1 mm Prepared by slip casting by pouring the slip in a petri dish	Sintering temperature: 550°C Soaking time: 5 h	Water	23–26 nm	3–7 vol%	–	Wang et al. 2001
α -Alumina powder (mean particle size of 21.2 μm) $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (LSCFO) powder	Circular disk support: Prepared by gel casting	Sintering temperature: 1450°C–1600°C Soaking time: 8 h	Acrylamide <i>N,N'</i> -methylene bis-acrylamide Ammonium bisulfate as initiator	0.90–3.65 μm	42.5–48.3 vol%	–	Meng et al. 2000
α -Alumina powder	Circular disk support: Diameter=23 mm Thickness=8 mm Prepared by gel casting by pouring in a nonporous mold	Sintering temperature: 1600°C Heating rate: 5°C/min Soaking time: 1 h	Dolapix CE64 as anionic polyelectrolyte dispersant Agar Locust bean gum	–	–	–	Olhero et al. 2000
α -Alumina powder γ -Alumina powder	Circular disk support: Diameter=30 mm Thickness=2 mm Prepared by pouring the slip into PMMA rings (Φ 66 mm) placed on a gypsum mold	For α -alumina powder: Sintering temperature: 1350°C Heating rate: 3°C/min Soaking time: 1 h For γ -alumina powder: Sintering temperature: 1350°C Heating rate: 10°C/min Soaking time: 16 h	PVA as binder and colloid stabilizer Diammonium hydrogen citrate as dispersing agent	1.5–2.4 μm (α -alumina) 3 μm (γ -alumina)	32–40 vol% (α -alumina) 58 vol% (γ -alumina)	–	Huang and Chen 1995
α -Alumina	Tubular support: ID=12 mm OD=14 mm Length=125 mm Prepared by slip casting	Sintering temperature: 1200°C (for α -alumina)	Darvan C as dispersant	0.1 μm	35 vol%	–	Hyun and Kang 1994

the starting alumina powder does not change the porosity (~33%). However, the pore size of the membrane fabricated with 600-nm particles is two times larger than the 300-nm particles, and the permeation resistance offered by the 600-nm particle membranes is lower than the 300-nm particle membranes. In 600-nm membrane supports, the percentage shrinkage (~13%) and the intermediate sintering stage temperature (100°C higher than the 300-nm particle) are found to be higher than the other membrane support. Many ceramic membrane supports and membranes were prepared by the filtration method, and most of the membrane supports reported in literatures are made up of high-purity α -alumina and zirconia (Somasundaran et al. 1999, Garrido and Aglietti 2001, Shqau et al. 2006, Maleksaeedi et al. 2008, Mottern et al. 2008).

Using the slip casting procedure, Hyun and Kang (1994) prepared an α -alumina support using a slurry (66.4%) in deionized water and Darvan C (NH_4^+PMA , which provides steric effects) as dispersing agent. They also prepared the titania supports (Hyun and Kang 1994) for membrane applications. The pore size of the α -alumina and titania membrane support was found to be 0.1 and 0.3 μm , respectively. Highly concentrated α -alumina slips (100 g α -alumina in 100 ml deionized water) were prepared using PVA (binder) and diammonium hydrogen citrate (additive and dispersing agent) by Huang and Chen (1995). The slurry (slipping solution) was milled in a ball mill, and the air bubbles were removed by vacuum suction and poured in to PMMA rings placed in a gypsum mold to obtain a membrane support. The detailed investigation reveals that the viscosities of the stable slips were strongly affected by the amounts of PVA added during the preparation of alumina slips. The rheological properties of the alumina slip vary with the amount of PVA content in the slip. The slip behaved as a Newtonian fluid at lower viscosity (<2%) and as a plastic fluid (non-Newtonian) at higher viscosities (>5%), and the well-dispersed slip was obtained at a pH value of 9.2 independent of the amount of PVA. Their results also revealed that varying the amount of PVA did not lead to any significant change in the mean pore diameter or shape of pore size distribution of the supports; however, the pore volume and porosity of the supports consistently increased with an increase in PVA amounts.

The centrifugal casting method is used to prepare tubular membrane supports from the slip solution subjected to a high centrifugal force. The largest particles present in the suspension move first to the mold wall followed by the smaller particles. The quality of the outer surface of the tubular support depends on the surface quality of the mold, whereas the inner surface of the

support depends on the suspension quality, especially the quantity of the smallest particles present in the suspension (Burggraaf and Cot 1996, Steenkamp et al. 2002). The speed of the centrifuge and the particle size distribution of the slip solution are the main parameters that affect the mean pore size of the membrane supports. Steenkamp et al. (2002) fabricated α -alumina membrane supports by centrifugal casting method using high-purity α -alumina powders (AKP-15 and AKP-30). The alumina powders were dispersed using Darvan C, and the suspension was stabilized by the addition of ammonia (pH=9.5). The above suspension was sonicated for 15 min before being poured to a stainless steel mold, which was then centrifuged for 20 min at 20 rpm to obtain a green support. Their detailed investigation on the membrane supports revealed that the α -alumina with higher mean particle diameter results in greater pore size (AKP-15: particle size=0.62 μm , pore size=0.1 μm ; AKP-30: particle size=0.40 μm , pore size=0.051 μm), which is attributed to the fact that bigger particles create more void space during packing. Due to the close particle packing (lower void space) of the α -alumina supports, the strength of the AKP-30 membrane supports are higher than AKP-15; the porosity of AKP-30 is lower than AKP-15 for the same reason. Mixing these two alumina using different ratios results in membrane supports with unpredictable relationships among pore size, porosity, and flexural strength, but with improved flexural strength and water permeability than pure AKP-15 membrane supports.

Gel casting is based on the theory of *in situ* polymerization of monomers on ceramic slurry, which forms a strong and cross-linked polymer-solvent gel after being poured into a mold (Prabhakaran et al. 1999, 2002, Liu et al. 2001). According to this process, ceramic powder is first dispersed into a water-based monomer solution to form a uniform slurry. Then, the catalyst and initiator are added to the slurry and poured in the mold of desired shape. Before filling the mold, the slurry must be deaerated, and it must be poured carefully to the mold to avoid the introduction of defects, which may affect the characteristics of the membrane support (Kong et al. 2007, Dong et al. 2013, Tulliani et al. 2013). The chemical cross-linking reactions form a strong hydrogel that permanently immobilizes the ceramic particle. The support is demolded, dried, and sintered to get the required membrane support. Porous ceramic supports are prepared by combining gel casting with foaming techniques or replica methods or the addition of a sacrificial phase (Liu et al. 2001, Ortega et al. 2003, Zhang et al. 2005). Pore size can be enhanced by increasing the organic material content. Porosity is usually <50%.

Xiang et al. (2002) fabricated an α -alumina membrane using a wide particle distribution of the α -alumina with a 55 vol% concentration in the slurry using gel casting method and investigated the pore size distribution of the membrane supports for the process parameters, such as the additives and pH value of the slurry, in terms of fluidity and stability of the slurry. They used kaolin powder, CaCO_3 , and SiO_2 as sintering aids, acrylamide as organic monomer, and methylene bisacrylamide as cross-linker. Ammonium persulfate was used as an initiator for polymerization reaction, and tetramethyl ethylenediamine was used as a catalyst. Dispersants and plasticizer were also used for the fabrication of the membrane support. Their studies revealed that an increased solid loading (55 vol%) was obtained for the slurry with dispersant compared with the slurry (solid loading=45 vol%) without dispersant. Viscosity increased with an increase in the amount of dispersant, and the optimum amount of dispersant needed to achieve the minimum viscosity of the slurry was found to be 1 wt%. It is obvious that low viscosity is beneficial for ease of fabrication and also enhances solid loading in the slurry. The appropriate pH value for the stable colloidal α -alumina slurry was found to be around 7–9.

Babaluo et al. (2004) fabricated ceramic supports using α -alumina (mean particle diameter=10 μm) by the gel casting method to obtain a membrane support with a mean pore diameter of 0.7 μm (pore size distribution range=0.3–1.16 μm). Their research work revealed that the mean particle diameter of α -alumina and its distribution decide its application as membrane supports or membranes.

The acrylate monomer in organic solvent was used in gel casting and was replaced with the acrylamide monomer in water in anticipation of environmental problems and additional costs concerned with the removal of the organic solvents. Two monomers are widely used: the main monomer (acrylamide), which has a single double bond and forms a linear polymer upon polymerization, and the second monomer, which is the cross-linking monomer [*N,N*-methylenebisacrylamide (MBAM)] and has at least two double bonds. When both are polymerized together, a cross-linked polymer-solvent gel is formed (Meng et al. 2000, Liu et al. 2001, Prabhakaran et al. 2002, Xiang et al. 2002). The highest health hazard rating (1, low; 2, moderate; 3, high; 4, extreme) of the monomers (acrylamide-4, MBAM-2) limits its commercialization. In addition, the difficulty in acquiring small pores with high porosity prevents the gel casting technique from becoming a universal production process. However, the recent research focused on natural polymers such as agar, agarose, gelatin,

sodium alginate, chitosan gels, egg white, proteins, and alginate from polysaccharides improved the possibility of the gel casting method for fabrication of membrane supports. Sintering additives such as Y_2O_3 and Yb_2O_3 have been separately used to fabricate porous Si_3N_4 ceramics. The challenge in gel casting lies in achieving a homogeneous suspension with high solid loading (>50 vol%) and viscosity (<1 Pa s). Many membrane supports have been fabricated by gel casting using different starting materials (Liu et al. 2001, Jia et al. 2002, Kong et al. 2007, Dong et al. 2013, Tulliani et al. 2013) and are reported in Table 2. Some special fabrication methods, such as electrodeposition (Mohammadi and Pak 2003), have also been used for the fabrication of the membrane supports by the colloidal processing method.

2.3 Paste processing method

Paste processing is one of the widely used traditional techniques for the fabrication of ceramic membranes. Membrane supports are fabricated by extrusion and manual pasting method, and extruded supports are most widely used for industrial applications. Unlike other fabrication methods discussed earlier, the majority of the membrane supports fabricated by the extrusion method are made of clays (Khider et al. 2004, Saffaj et al. 2004, Mohammadi et al. 2005, Bouzerara et al. 2006, Dong et al. 2006, Kazemimoghadam and Mohammadi 2007, Khemakhem et al. 2007, Jedidi et al. 2009). This is attributed to the plastic properties (rheology) of the clays. Clay readily forms paste and can be easily extruded to the desired shape with lower extrusion pressure. The processing of inorganic ceramics by mixing with binders, plasticizers, lubricants, etc., as additives, gives the required plastic properties that provide excellent shape-forming capabilities without losing its cohesion. Usually, cellulose derivatives (methylcellulose, carboxymethylcellulose, hydroxyethyl cellulose, etc.) are used as binders, organic polymers (PVA, PAA, PEG, etc.) are used as plasticizers or lubricants, and a starch derivative, especially corn starch, is used as the pore-forming agent (Benito et al. 2005, Bouzerara et al. 2006, Wang et al. 2007, Qi et al. 2010).

In the extrusion method, the homogeneous paste is forced through the opening of a die with the help of an endless screw, especially auger or extruder (in industry) or a piston (in the laboratory). Ceramic membranes are fabricated with various specifications (e.g., the number of channels, diameter of channels, external diameter of the tubes) by changing the geometry of the die. Tubular and multichannel membrane supports have been widely

prepared by this method (Burggraaf and Cot 1996, Tsuru 2001). The high surface-to-volume ratio of the modules provides good opportunity to process large feed rates. Due to this reason, the membranes have enhanced implementation in industries. The most important parameters that determine the membrane properties (mean pore size and porosity) are particle size of the ceramic or clay powder, nature and proportion of organic additives, pugging and ageing of the paste, extrusion pressure, and velocity. Larbot and colleague (Khider et al. 2004, Saffaj et al. 2004) fabricated a tubular support by extrusion method using Algerian clay (attapulgate) and cordierite powder as starting raw material. They used methylcellulose (Methocel) as binder and plasticizer, Amigel as deforming agent, and corn starch as pore-forming agent. Benito et al. (2005) fabricated a membrane support using an α -alumina or cordierite reactive mix with PEG as plasticizer. Typically, most of the fabrication methods use organic binders or plasticizers for paste preparation; however, a few works reported on support fabrication with inorganic precursors for paste preparation. Mohammadi et al. (2005) fabricated a kaolin membrane support using alumina as sintering aid and sodium carbonate as pore former and paste conditioner. They also followed Taguchi's procedure to reduce the number of experiments, which reduces the cost and time. Their main intention is to develop a mullite support because it has outstanding properties, such as low thermal conductivity and expansion, excellent creep resistance, and excellent thermal, chemical, and mechanical stability. In addition, it retains porosity at elevated temperatures. Their investigation revealed that addition of alumina enhances the mullite formation and the increase in the amount of sodium carbonate increases the porosity due to CO_2 formation during sintering. In addition, the formation of a glassy phase during sintering would block the pores, resulting in decreased porosity and permeability. Bouzerara et al. (2006) prepared the membrane support using kaolin and dolomite mixtures to reduce the cost of the membranes. The supports were prepared by four different methods, namely, roll pressing, dry pressing, pasting to tubular, and plane configuration. Their investigation revealed that the pore structures (modal distributions of pore size, total porosity, and average pore size) are mainly dependent on sintering temperature, additives, and processing routes and could be controlled by controlling these parameters. Recent research by Jedidi et al. (2009) revealed that membrane support with good porosity (51%) and a median pore size of $4.5 \mu\text{m}$ could be successfully fabricated with low-cost fly ash as a starting raw material using the extrusion method. Many works reported on the use of kaolin in the fabrication of low-cost

membrane supports, which is due to its unique characteristics toward membrane applications (Saffaj et al. 2004, Mohammadi et al. 2005, Bouzerara et al. 2006, Dong et al. 2006, Kazemimoghadam and Mohammadi 2007, Khemakhem et al. 2007).

Numerous research works have focused on the development of kaolin-based supports by mixing with other sintering aids, such as alumina, quartz, ball clay, feldspar, calcium carbonate, magnesium carbonate, sodium carbonate, talc, titania (rutile), and fly ash, to enhance the porosity and mechanical strength of the membrane support (Zeng et al. 1998, Almandoz et al. 2004, Benito et al. 2005, Mohammadi et al. 2005, Bouzerara et al. 2006, Dong et al. 2006). Membrane supports fabricated by paste processing is presented in Table 3.

In the manual pasting method, the membrane supports are fabricated manually on a flat porous (gypsum) or nonporous surface. The pressure is applied manually to form the required shape. It is the simplest and the oldest technique compared with other fabrication methods and does not require any instrument for fabrication. However, controlling the microstructure (to produce optimum reproducible results) is a hard challenge and requires skills to achieve membrane supports without defects. Kumar and colleagues (Potdar et al. 2002, Neelakandan et al. 2003, Sachdeva and Kumar 2008) fabricated kaolin supports using low-cost ceramic clay mixtures, and these kaolin supports have various liquid separation applications. A similar type of ceramic clay mixtures were also used by other researchers for the fabrication of ceramic membrane supports (Almandoz et al. 2004, Belouatek et al. 2005, Nandi et al. 2008).

The advantages and disadvantages of the various support fabrication techniques are summarized in Table 4. A list of the commercial membrane supports used for membrane applications are also listed in Table 5. Although various commercial ceramic membranes are available today, there are very few detailed reports on the fabrication of ceramic membrane supports because the techniques were considered commercial/trade secrets. In general, the transport properties of the membrane supports depend on pore structure parameters such as open porosity, pore shape, pore size, and its distribution. These are mainly influenced by the fabrication method, starting raw material, and sintering conditions. In summary, most of the ceramic supports are routinely prepared using high-purity expensive powders as starting materials with the combustion of organic pore-forming agents. Recent research on kaolin and mullite ceramic support showed good mechanical stability and surface properties. In the near future, one can expect that kaolin- and mullite-based

Table 3 Membrane supports fabricated by paste processing method.

Support materials (mean particle diameter is in parentheses)	Support details	Sintering details	Additives	Pore size	Total porosity	Bending strength	Reference
Mixture of clay powder Prepared by extrusion method	Tubular support:	Sintering temperature: 1300°C Soaking time: 1 h	Calcium carbonate (21 wt%) Amijel (2.5 wt%) derived from methylcellulose Methocel (2.5 wt%) derived from starch Water	4.89 μm	52 vol%	–	Bouzerara et al. 2012
α-Alumina (6.1 μm) Kaolin (6.8 μm) Prepared by extrusion method	Capillary tube support: ID=1.9 mm OD=3.1 mm	Sintering temperature: 1200°C–1450°C Soaking time: 1.5 h	Methocel as plasticizer Amijel as a binder Corn starch as pore-forming agent Water to form raw paste	1.1–1.5 μm	49–50 vol%	14–27 MPa Three-point bending test Span length: 30 mm Cross-head speed: 10 mm/min	Sarkar et al. 2012
α-Alumina (20 μm) Prepared by extrusion method	Tubular support: ID=8.91 mm OD=13.8 mm Length=80 mm	Sintering temperature: 1620°C Soaking time: 2 h	Kaolin clay (5 wt%) as a paste plasticizer Corn starch (8 wt%) as pore-forming agent	2.96 μm	39.80 vol%	87 MPa Three-point bending test Test specimen size: 40×5.92×3.2 mm (bar type) Span length: 30 mm Cross-head speed: 0.5 mm/min	Dong et al. 2011
Perlite powder Prepared by extrusion method	Flat disk support: Diameter=44 mm	Sintering temperature: 1000°C Heating rate: 15°C/min	Methocel (4%) Amijel (4%) as binder Corn starch (10%) as pore-forming agent PEG 1500 as binder Zusoplast (0.24%) as lubricant	6.64 μm	42 vol%	1.2 MPa	Majouli et al. 2011
Fly ash (15.41 μm) Prepared by extrusion method	Tubular support: ID=5.5 mm OD=10 mm Length=100 mm	Sintering temperature: 1190°C Heating rate: 3°C/min Soaking time: 2 h	Methylcellulose and water	2.13 μm	–	–	Fang et al. 2011
α-Alumina (30 μm) Titania (0.5 μm) Prepared by extrusion method	Tubular support: ID=8 mm OD=12 mm	Sintering temperature: 1400°C Heating rate: 3°C/min Soaking time: 2 h	Carboxymethylcellulose as binder PVA (10 wt%) as plasticizer	6.8 μm	42 vol%	32.7 MPa Three-point bending test Test specimen size: 120×12×8 mm (tubular support) Constant loading rate of 550 N/min	Qi et al. 2010

(Table 3 Continued)

Support materials (mean particle diameter is in parentheses)	Support details	Sintering details	Additives	Pore size	Total porosity	Bending strength	Reference
Fly ash Prepared by extrusion method	Tubular support:	Sintering temperature: 1100°C–1130°C	Methocel (4%) Amijel (4%) Starch (8%)	4.5 μm	51 vol%	22.9 MPa Three-point bending test Test specimen size: 32×10×2 mm (bar type) Span length: 28 mm	Jedidi et al. 2009
Rutile titania (1.85 μm) Prepared by extrusion method	Tubular support: OD=12 mm Length=250 mm	Sintering temperature: 600°C–900°C Soaking time: 2 h	PAA (PAA5000) or PEG (PEG800)	2.10 μm	43 vol%	–	Wang et al. 2008
Kaolin Ball clay Feldspar Quartz Pyrophallite Calcium carbonate Prepared by manual molding method	Circular disk support: Diameter=76 mm Thickness=4 mm Support fabricate over gypsum surface	Sintering temperature: 1000°C Heating rate: 10°C/min Soaking Time: 8 h	–	–	–	–	Sachdeva and Kumar 2008
Kaolin Ball clay Quartz Boric acid Calcium carbonate Sodium carbonate Sodium meta silicate water	Circular disk support: Diameter=55 mm Thickness=5 mm Support fabricate over gypsum surface	Sintering temperature: 850°C–1000°C Heating rate: 2°C/min Soaking Time: 8 h	–	0.55–0.81 μm	33–42 vol%	3–8 MPa Three-point bending test	Nandi et al. 2008
Cordierite powder (range of particle diameter: 100–250 μm) Prepared by extrusion method	Tubular support:	Sintering temperature: 1300°C–1400°C Soaking time: 2 h	Kaolin (K) and basic carbonate magnesium (M) as sintering aid (K/M=3.25:1) Corn starch as pore-forming agent Methylcellulose (MC-400) as binder	8.66 μm	36 vol%	31.03 MPa Three-point bending test Span length: 30 mm Cross-head speed: 0.5 mm/min	Dong et al. 2007

(Table 3 Continued)

Support materials (mean particle diameter is in parentheses)	Support details	Sintering details	Additives	Pore size	Total porosity	Bending strength	Reference
Tunisian Clay Prepared by extrusion method	Tubular support: ID=7 mm OD=10 mm Length=20 mm	Sintering temperature: ~1100°C Soaking time: 2 h	Organic Binders	6.3 μm	48 vol%	–	Khemakhem et al. 2007
Titania (rutile powder with a median particle diameter of 10.31 μm) Prepared by extrusion method	Tubular support: OD=12 mm Length=250 mm	Sintering temperature: 1400°C Heating rate: 1°C/min Soaking time: 2–8 h	methylcellulose as binder Corn starch as pore-forming agent	2.10 μm	43 vol%	20 MPa Three-point bending test Test specimen size: 60×5×5 mm (bar type)	Wang et al. 2007
Kaolin clay Prepared by extrusion method	Tubular support: ID=10 mm OD=14 mm Length=150 mm	Sintering temperature: 1250°C Soaking time: 3 h	–	–	–	–	Kazemimoghdam and Mohammadi 2007
Barbotine powder (mixture of kaolin, feldspar, and sand with a median particle diameter of 1–40 μm) Prepared by manual molding method	Tubular support: ID=15 mm OD=19 mm Length=200 mm	Sintering temperature: 1100°C Heating rate: 10°C/min Soaking time: 7 h	Na ₂ CO ₃ as deflocculant	0.9 μm	15 vol%	–	Belouatek et al. 2005
α-Alumina Prepared by extrusion method	Tubular multilayer MF membranes: OD=32 mm Length=250 mm	Sintering temperature: 800°C Soaking time: 2 h	PAA (PAA5000) or PEG (PEG800)	0.30 μm	–	–	Wang et al. 2006
Kaolin Dolomite Prepared by extrusion method	Tubular and flat support	Sintering temperature: 1000°C–1300°C Heating rate: 4°C/min Soaking Time: 1 h	Methylcellulose (4 wt%) as a plasticizer Amijel (4 wt%) as a binder.	0.02–7.68 μm	37–56 vol%	16 MPa Diametral compression test Cross-head speed: 0.2 mm/min	Bouzerara et al. 2006
Cordierite powder (100–315 μm) Kaolinite Magnesium carbonate Prepared by extrusion method	Tubular support	Sintering temperature: 1380°C Soaking Time: 4 h Heating and cooling rate: 3°C/min	Corn starch as pore-forming agent Methylcellulose as organic binder Water, glycerol, surfactant, and lubricant	18 μm	41 vol%	28.7 MPa Three-point bending test Test specimen size: 50×3×3 mm (bar type) Span length: 40 mm Cross-head speed: 0.001 mm/min	Dong et al. 2006

(Table 3 Continued)

Support materials (mean particle diameter is in parentheses)	Support details	Sintering details	Additives	Pore size	Total porosity	Bending strength	Reference
Kaolin Alumina (150 μm) Sodium carbonate Prepared by extrusion method	Tubular support: ID=8 mm OD=15 mm Length=150 mm	Sintering temperature: 1100°C–1300°C Soaking Time: 3–5 h	–	5.5 μm	39 vol%	–	Mohammadi et al. 2005
α -Alumina powder and cordierite reactive mix (formed by talc, kaolinite, and magnesite) Prepared by extrusion method	Two different supports in tubular form	Sintering temperature: 1600°C Heating rate: 5°C/min Soaking Time: 2 h	Carboxymethylcellulose as binder PEG (1000 g/mol) as plasticizer	1.2 and 10 μm	35 and 45 vol%	–	Benito et al. 2005
Cordierite powder (particle size range=0–125 μm) Prepared by extrusion method	Tubular-shaped support:	Sintering temperature: 1275°C	Organic additives	7 μm	40 vol%	–	Saffaj et al. 2004
Algerian clay (attapulgite) Prepared by extrusion method	Tubular-shaped support: OD=14 mm Length=20 mm	Sintering temperature: 900°C	Methocel as binder Amigel as deforming agent Starch as porosity agent	1.22 μm	48 vol%	–	Khider et al. 2004
Kaolin Ball clay Feldspar Quartz Pyrophallite Calcium carbonate Prepared by manual molding method	Circular disk support: Diameter=39 mm Thickness=2 mm Support fabricate over gypsum surface	Sintering temperature: 900°C Soaking Time: 8–10 h	–	0.08 μm	36 vol%	–	Potdar et al. 2002
α -Alumina powder (mean particle size=0.5 and 2.8 μm) Prepared by extrusion method	Tubular-shaped support ID=8 mm OD=10 mm Length=100 mm	Sintering temperature: 1100°C–1300°C Heating rate: 3°C/min	Binder+dispersant (details not given)	8 μm	41 vol%	–	Wang et al. 1999

Table 4 Advantages and disadvantages of various support fabrication methods.

Fabrication method	Advantages	Disadvantages
Powder pressing method	Uniaxial pressing <ul style="list-style-type: none"> – Simple and cost-effective – Ease of fabrication – High production rate – Fewer controlling parameters (controlling parameters such as pH, solvent-to-feed ratio or slurry concentrations, paste concentration, etc. are major concern for other processing methods) – Less shrinkage of the green supports after sintering – Lower drying time – Higher heating rate does not affect pore characteristics significantly Isostatic pressing (hot and cold) method <ul style="list-style-type: none"> – Fabrication of tubular supports and other configurations are possible – Possibility of defect is less due to uniform pressure distribution – Greater uniformity of compaction – Increased shape capability 	<ul style="list-style-type: none"> – Fabrication is restricted to flat-shaped membrane supports (disk-, rectangular-, or square-shaped) – More chances of defect formation due to air entrapment – Die wear and uneven pressure distribution
Colloidal processing method	Slip casting method <ul style="list-style-type: none"> – Suitable for fabrication of all complicated shapes (e.g., star-, disk-, tubular-shaped) – No instruments are required for fabrication – Drying and heat treatment process are more time consuming – Shrinkage of the support after sintering is more. – Low heating rate must be maintained to get a proper support without bending Centrifugal casting method <ul style="list-style-type: none"> – Highly stabilized sol is not required for the formation of tubular supports – Gradual increment in the pore size Gel casting method <ul style="list-style-type: none"> – Gel cast membrane supports has high strength. So it can be easily shaped before sintering – Gelation gives a high dense membrane support, hence used as a standalone membrane rather than support 	<ul style="list-style-type: none"> – Dense membrane supports can be obtained. Used for microfiltration application. Hardly used as membrane support. – Complication in the press operation – Energy consumption is more than the uniaxial pressing – Very slow and more expensive process – Difficult to maintain controlling parameters of the colloidal sol – Chemicals requirements are high to produce stable colloidal sol – Environmental, safety, and health hazards involved in using the precursors of the colloidal sol – Fabrication is restricted to tubular-shaped membrane supports – Always inside pore diameter is always lower than the outside pore diameter. So selective layer will be always prepared in the inside of the tubular support. – Difficulty in removing the fabricated green support – More precursors are required for the fabrication – Prolonged drying time, hence the production rate is low – Prolonged heating for binder burnout – Environmental, safety, and health hazards involved in few monomer and polymer for gelation

(Table 4 Continued)

Fabrication method	Advantages	Disadvantages
Paste processing method	Extrusion method – Tubular membranes are produced at higher production rates – Low-cost clays can be processed to obtain high-quality tubular membrane supports	– Higher fabrication cost, high energy consumption (due to the higher operating cost of the extruder) – Difficulty in maintaining the rheology of the paste (especially during pugging and ageing)
Manual molding method	– Simple and cost-effective – Ease of fabrication – No complicated instruments required	– Difficult to maintain the plastic behavior of the paste – Reproducibility is a major concern. Hands on experience required – Fabrication is limited to disk or flat shapes – Long drying time – Higher tendency to bend; thus, a lower heating rate must be maintained to get a proper support

Table 5 List of commercial membrane supports used for membrane applications.

Support material	Commercial producer	Details of the membrane support	Reference
α -Alumina	Franhofer, Germany	Flat sheet support: Diameter=50 mm Thickness=1 mm Pore size=0.2 μ m	Mendret et al. 2013
α -Alumina	Sterilitech Corp., USA	Circular/disk-shaped support: Diameter=47 mm Thickness=2.5 mm Pore size=0.2 μ m	Lee et al. 2013
α -Alumina	Hyflux Membrane Co., Singapore	Hollow fiber support: ID=2.5 mm OD=3.5 mm Length=30 mm Pore size: 2 μ m Porosity=30–40 vol%	Zhou et al. 2013
α -Alumina	Jiangsu Jiuwu Hi-Tech, China	Tubular-shaped support: ID=8 mm OD=12 mm Length=100 mm Pore size: 0.2–0.5 μ m	Li et al. 2012
α -Alumina	Atech innovations GmbH, Germany	Tubular-shaped support: ID=8 mm OD=14 mm Pore size: 0.2–0.5 μ m	Dhariwal et al. 2008
Titania	TAMI Industries, France	Tubular-shaped support: Pore size: 1.7 μ m porosity=32 vol%	Wang et al. 2008
α -Alumina	Pall corporation, USA	Tubular-shaped support: OD=10 mm Length=80 mm Pore size=1.0 μ m Porosity=40 vol%	Li et al. 2008
α -Alumina	Membralox Membrane (T 1.70), USA	Tubular membrane with three concentric layers of α -alumina: Layer 1: Thickness=1.5 mm Pore diameter=12 μ m Layer 2: Thickness=0.04 mm Pore diameter=0.8 μ m Layer 3:	Haag et al. 2006

(Table 5 Continued)

Support material	Commercial producer	Details of the membrane support	Reference
Titania support	Fine Continents (USA) Corporation, Newark, NJ, USA	Thickness=0.02 mm Pore diameter=0.2 μ m Tubular support Dimension not mentioned	Ahmad et al. 2006
Not mentioned	Courtesy of Fairey Industrial Ceramics Ltd., UK	Star-shaped tubular ceramic membrane support: ID=2.8 mm OD=4.6 mm Length=300 mm Pore size=0.35 μ m	Chiu and James 2006
α -Alumina	Whatman Anopore Filters, USA	Circular/disk-shaped support: Diameter=47 mm Thickness=50 μ m Pore size=0.2 μ m	Zhang et al. 2006
α -Alumina	Netsch, USA	Tubular channel support: 19 channels Permeation area=0.2 m ² Pore size=10 nm	Basso et al. 2006
α -Alumina	NOK Co., Japan	Tubular-shaped support: OD=2.7 mm Length=50 mm Pore size=0.1 μ m Porosity=40 vol%	Nomura et al. 2006
α -Alumina	Membralox T1-70	Tubular-shaped support: Pore diameter=30 and 50 nm	Beolchini et al. 2006
Tubular AZT (a mixture of alumina, zirconia, and titania)	CeRAM, TAMI, Canada	Ceramic membrane with clover-leaf design: OD=10 mm Length=80 mm Pore size=kDa	Karnik et al. 2005
α -Alumina+titanium	TAMI Industry, Lyons, France	Rectangular-shaped membrane support: Dimension: 7.5 \times 2.5 \times 2.5 mm Pore size: 1.0 μ m Porosity=35 vol%	Fievet et al. 2003
α -Alumina	Schumacker GmbH, Germany	Tubular-shaped support: ID=7 mm OD=10 mm Length=250 mm Pore size=0.2 μ m	Tavolaro 2002

(Table 5 Continued)

Support material	Commercial producer	Details of the membrane support	Reference
α -Alumina	Dongsuh Company, Korea	Tubular-shaped support: ID=6.0 mm OD=7.2 mm Length=28 mm Pore size=1.0 μ m Porosity=4 vol%	Kang and Gavalas 2002
α -Alumina	Inocermic and SCTJ, France	Tubular-shaped support: ID=7 mm OD=10 mm Length=30–50 mm Pore size=5, 200, 500 nm	Bernal et al. 2002
α -Alumina	Sen Bool Sintering Co., Korea	Tubular-shaped support: Pore size=10 μ m	Hwang et al. 2001
α -Alumina	Velterop BV, The Netherlands	Circular/disk-shaped support: Diameter=25 mm Thickness=2 mm Available pore sizes: 0.08, 0.15, 2, and 9 μ m Tubular-shaped support: ID=8 mm OD=14 mm Available pore sizes: 2.5 and 9 μ m	Romanos et al. 2001
γ -Alumina	US Filters, USA	Tubular-shaped support: ID=7 mm OD=10 mm Length=55 mm Pore size=5 nm	Tsai et al. 2000
α -Alumina	NGK Insulators, Ltd., Japan	Circular/disk-shaped support: Diameter=12 mm Pore size=0.1 μ m	Matsufuji et al. 2000
α -Alumina with an inner layer of α -alumina	US Filters, USA	Tubular-shaped support: ID=7 mm OD=10 mm Pore diameter=200 nm	Tuan et al. 1999
α -Alumina tubular membrane with an γ -Alumina inner surface	US Filters, USA	ID=6.5 mm OD=10 mm Length=84 mm Pore diameter=5 nm (γ -alumina)	Jia et al. 1994

membranes would be commercialized for various industrial applications.

3 Conclusion

Porous ceramic membrane supports are reviewed from the viewpoint of membrane fabrication methods. Fabrication of porous ceramic membrane support has been classified into three major categories: powder processing, paste processing, and colloidal processing. The characteristics of the porous supports hold considerable promise in applications such as separation of species from aqueous or nonaqueous systems and for systems operating at high

temperatures. The different strategies followed for the fabrication of ceramic supports ended with different surface characteristics, which plays an important role in membrane performance. The affinity of the selective layer over the support layer differs based on the fabrication method, even with the same starting raw materials. Further investigation is required to understand the effect of support layer on the formation of selective layer without defects. Increasing research on mullite-based membrane supports indicates that it would definitely become another alternative for α -alumina, zirconia, titania, and other commercial membrane supports.

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