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INORGANIC POROUS MEMBRANES FOR LIQUID PHASE SEPARATION

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INORGANIC POROUS MEMBRANES FOR LIQUID PHASE SEPARATION

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ABSTRACT

Porous ceramic membranes are reviewed with reference to liquid phase separation. Methods for preparing porous ceramic membranes are summarized after a brief introduction to membranes and membrane processes. In the section on liquid phase separation, membrane materials are summarized from the viewpoint of pore size limits, since the pore sizes of porous mem-

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branes play an important role in determining separation performance. Various types of metal oxides and composite oxides have been developed by the sol-gel process; typical materials are Al_2O_3, TiO_2, SiO_2, ZrO_2, and composite oxides. The sol-gel process has a great advantage in terms of pore-size controllability over a wide range, from 0.5 ~ several ten nm, and therefore, is suitable for preparing membranes for use in liquid phase separation. Applications of inorganic membranes are reviewed in terms of water treatment, separation of nonaqueous systems, and photocatalysis.

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1. INTRODUCTION

A general definition of a membrane is that it is “a selective barrier between two phases” [1]. Therefore, using membranes, the feed is separated into two streams, i. e., the retentate and permeate streams, as shown in Fig. 1. Either the retentate or the permeate could be product stream, depending upon types of membranes used and the feed stream. The permeate stream is the product stream, if the solvent is purified by removing solutes using a membrane which allows the permeation of solvent and retains the permeation of solutes, such as in the desalination of seawater. If the purpose of the separation process is the concentration of solutes, then the retentate becomes the product.

Membrane separation, which is a relatively new separation process, has been commercialized in the last two decades. The majority of membrane materials which have been commercialized thus far are polymeric. Porous ceramic membranes have great potential for opening up new types of applications to which polymeric membranes cannot be applied. This review will summarize the present status and a potential application of porous ceramics as materials for membrane separation.

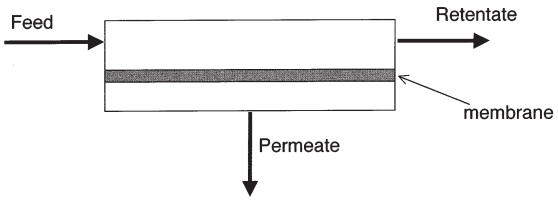

Figure 1. Membrane separation process (feed stream is divided into retentate and permeate).

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2. PREPARATION OF POROUS CERAMIC MEMBRANES

Membrane separation processes can be categorized based on the phases of the feed and permeate, as well as the types of driving force for the separation, as shown in Table 1 [1]. For the case where both the feed and permeate streams are a liquid phase and the driving force is a pressure difference between the two phases, the separation process is referred to a filtration process such as microfiltration (MF), ultrafiltration (UF), and nanofiltration (NF), and reverse osmosis (RO). It should be noted that membranes, the pore sizes of which are larger than 10 μm, are usually categorized as filters. Gas separation is conducted in the gas phase for both feed and permeate stream. For the case of pervaporation, the feed

Table 1. Membrane Processes Based on Phase and Driving Force

	Phase				
Membrane Process	Feed	Permeate	Driving Force	Pore Size	Note
Microfiltration	L	L	ΔP	0.1∼10 μm	Removal of particles
Ultrafiltration	L	L	ΔP	2∼100 nm	Separation of macromolecules
Nanofiltration	L	L	ΔP	1 ∼ 2 nm	Separation of low MW solutes (MWCO 200 ∼1,000); electrolyte separation by surface charge
Reverse osmosis	L	L	ΔP	< 1 nm	Reject electrolytes; solution-diffusion mechanism (polymeric membranes)
Gas separation	G	G	ΔP	< 0.5∼1nm	
Vapor permeation	G	G	ΔP	< 0.5∼1nm	
Pervaporation	L	G	ΔP	0.5∼2nm	
Electrodialysis	L	L	ΔΦ		
Dialysis	L	L	ΔC		
Membrane distillation	L	L	ΔT		

L: liquid phase, G: gas phase.
ΔP: (partial) pressure difference, ΔΦ: electrical potential difference, ΔC: concentration difference, ΔT: temperature difference.

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stream is a liquid phase, while the permeate stream is a gas phase by evacuation. Other separation processes (electrodialysis, dialysis, membrane distillation) are also conducted in the liquid phase, but ceramic porous membranes have not yet been applied to these types of separation processes. The separation mechanism is mainly controlled by the sieving effects, where molecules which are smaller than the pore sizes of membranes permeate through the porous membranes. Another mechanism is the affinity (such as selective adsorption and diffusion) of molecules with membrane materials, but this mechanism plays an important role in cases where the pore size is relatively small.

Most applications have been carried out using polymeric membranes, while inorganic membranes, including ceramic membranes, have been utilized to some extent in practical applications. For example, inorganic micro- and ultrafiltration membranes, which are currently commercially available, have been applied in areas of food, beverage, and biotechnology, and comprise approximately 12 % of the membranes used in these applications [2]. As shown in Table 2, inorganic materials have the advantages of thermal stability, resistance to solvents and chemicals. It should be noted that the advantages are dependent on the types of materials used. Mechanical strength and long life-time are also one of the advantages of ceramic over polymeric materials [2, 3]. Inorganic membranes have the disadvantage of difficulty in sealing between the inorganic membranes and metal housings, and constructing modules, and also are considered to have a relatively high cost because of the expensive source materials, the complex processing of membrane fabrication, and low membrane surface area per volume of a membrane module (low packing density compared with polymeric membranes). The selec-

Table 2. Advantages and Disadvantages of Inorganic Membranes

Advantages/ Disadvantages	Applications and Comments
Advantages	
Thermal stability	Separation at high temperature, steam sterilization
Resistance to organic solvents	Separation of non-aqueous systems, separation of oil
Resistance to chemicals, acidic and alkali pH	Chemical cleaning, recovery of acid/ basic
Resistance to peroxide	Chemical cleaning, application of textile processing
Mechanical strength	Back-washing
Long life time	
Uniform pore size	Dependent upon preparation methods
Disadvantages	
Difficult sealing and module construction	
Cost	Expensive source materials, complex processing

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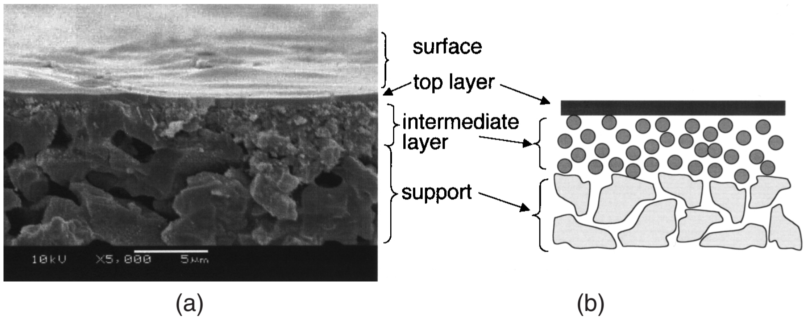

Figure 2. SEM photo (a) and a schematic representation (b) of an asymmetric-composite membrane.

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tivity of inorganic membranes is considered to be rather low compared with polymeric membranes, but recently it has been made clear several inorganic membranes show superior separation characteristics, compared to conventional polymeric membranes.

Porous membranes must have pores which are connected continuously from the feed stream to permeate stream, otherwise no permeation through the membranes is possible. Figure 2 shows a SEM photo and a schematic representation of a typical structure of porous membranes: asymmetric-composite membranes. Porous supports, which are usually manufactured using powders by extrusion or slip-casting, have large pore sizes in excess of 1 μm and a thickness of the order of mm, and are designated for purposes of mechanical strength. The intermediate layer is coated on the support layer to reduce pore sizes for the further coating of the top layer. The separation top layer, which has separation ability and needs to have controlled pore sizes suitable for the specific separation, is formed as thin as possible on the intermediate layer. In this way, the pore size of asymmetric composite membranes shows a gradient structure from porous supports to the separation layer, so as to minimize the resistance to permeation across a membrane.

Table 3 summarizes the preparation processes of inorganic membranes and the pore size limits [2, 3]. Membranes can be classified into two groups based on differences in their morphology: porous or nonporous membranes. In powder sintering methods, ceramic powders, which have been pre-ground to several μm in diameter, can be formed in various types of membrane shapes such as tubes, plates and monoliths, by extrusion, tape-casting, and slip-casting. Since there is a low limit of particle diameters at approximately several hundred nm, the pore sizes of the membranes are approximately 0.1 μm at a minimum, which is in the microfiltration range, and are not small enough for molecular separation. Therefore, membranes prepared by powder sintering have been used as supports for preparing membranes of small pore sizes by further coating.

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Table 3. Preparation Methods of Inorganic Membranes

Type	Process	Materials	Pore Diameter
Porous membranes	Powder sintering (extrusion or tape-casting)	αAl_2O_3, ZrO_2, TiO_2	100 nm ∼
	Sol-Gel	SiO_2, γAl_2O_3, ZrO_2, TiO_2, Fe_2O_3	1 ∼ 50 nm
	CVD	SiO_2	$<$ 1 nm
	Pyrolysis	C, SiC, Si_3N_4	$<$ 1 nm
	Hydrothermal treatment	Silicalite, NaA, NaY	$<$ 1 nm
	Anodic oxidation	Al_2O_3(amorphous)	10 nm ∼
	Phase separation/ leaching	SiO_2	4 nm ∼
	Dynamic membranes	Amorphous ZrO_2	
	Metal	Sintered stainless steel	100 nm ∼
Non-porous membranes	Solid electrolyte	YSZ, perovskite	
	Metal	Pd, Pd/Ag	
	Modification with organic component	Silane coupling agent	
Composite membranes	Modification with inorganic component	MgO, Ag	

Porous membranes have been prepared by the sol-gel process from a variety of metal oxides and composite oxides. The sol-gel process is divided into two main routes: the polymeric sol-gel routes and the colloidal sol-gel route, as shown in Fig. 3. A metal alkoxide or inorganic salt is hydrolyzed and a simultaneous condensation reaction occurs to form polymeric or colloidal sols. In the colloidal sol route, the hydrolysis and condensation reaction is fast, in comparison with the case of the polymeric sol route, which is achieved by adjusting the reaction conditions (type of alkoxide, solvent, catalyst, composition of reactants, molar ratio of water, temperature, etc.), resulting in a fully hydrolyzed alkoxide (highly branched polymer). The rapid condensation reaction causes particulate growth and/ or the formation of precipitates. Particulate sols can be obtained by the precise control of reaction conditions and/or the peptization of the precipitate by adding acid. In the polymeric sol route, the hydrolysis reaction is kept slower and typically achieved by adding a small amount of water, resulting in a

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partially hydrolyzed alkoxide and the formation of a linear inorganic polymer. Through the subsequent gellation process, polymeric sols form a gel network. In both routes, the pore size of membranes can be controlled by the size of the sols; pore sizes can be controlled by the void spaces among the packed colloidal particles (i. e. interparticle pore) for the case of the colloidal sol route and the size of the gel network for the case of the polymeric gel route, respectively. Since the size of the gel network is smaller than the size of colloidal sols, the polymeric sol route is thought to be appropriate for the preparation of microporous materials. Pore sizes by the sol-gel process can be controlled from less than 1 nm to approximately 50 nm. Materials prepared have been silica, γ-alumina, titania, zirconia, and composite oxides such as silica-zirconia, and will be discussed extensively in a later section.

Chemical vapor deposition (CVD) of metal alkoxides such as tetraethoxysilane (TEOS) has been carried out to prepare microporous membranes, the pore sizes of which are controlled less than 0.5 nm, which is suitable especially for hydrogen separation [4, 5, 6]. A pyrolysis method is also employed for the preparation of microporous membranes [2, 3, 7]. Polyimide, polyvinylidene chloride, cel-

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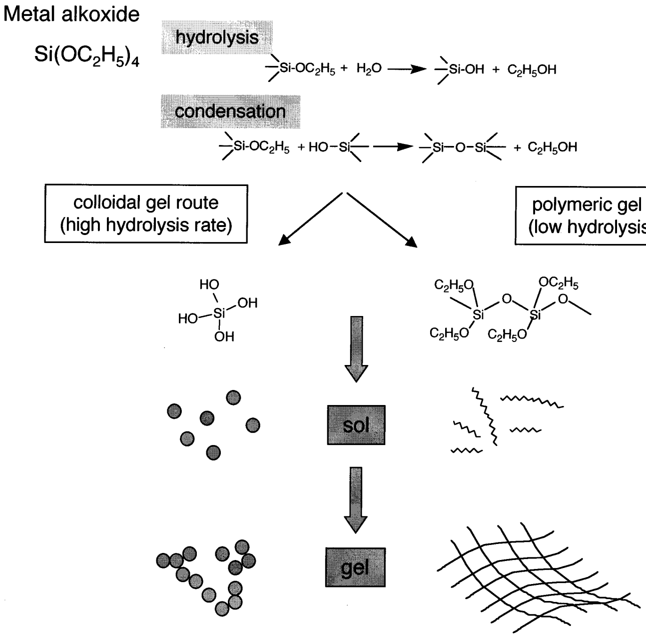

Figure 3. Colloidal and polymeric routes of sol-gel processing using metal alkoxide.

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lulose, polyacrylonitrile, and phenolic resin, which are thermosetting polymers or have high melting points, have been pyrolyzed in the absence of oxygen at high temperature in a range from 600–800°C, in a form of supported membranes or self-standing fibers such as hollow fibers. The pore size is less than 1 nm, and shows gas separation ability such as oxygen/nitrogen. Zeolite or zeolitic membranes have been prepared by hydrothermal treatment. To date, MFI (silicalite and ZSM-5), A, and Y-type zeolite membranes have been reported to be successfully manufactured [8–11], and some are currently commercially available. The pore sizes of zeolite membranes are basically determined by the crystalline intrapores (zeolitic pores), and therefore usually less than 1 nm. It should be noted that the separation mechanism of zeolite membranes remains controversial, as to whether the permeation is controlled by zeolitic intrapores or intercrystalline pores. Anodic oxidation of aluminum in acid solutions gives uniform cylindrical pores as shown in Fig. 4 [12], which is different in structure from membranes prepared by other methods, but the pore size is normally larger than 10 nm.

In phase separation and leaching method [13–15], a homogeneous glass such as ternary mixtures of SiO_2—B_2O_3—Na_2O is melt at high temperature (1000–1500°C), separates into two phases: a silica-rich and poor phase, after leaving at a specified temperature, based on spinodal demixing. After leaching the silica-poor phase by acid, a porous silica membrane can be obtained. The typical membrane is a Vycor glass porous membrane, which has pore size of 4 nm. A pore size by this method can be reduced to approximately 0.5 nm by the precise control of the conditions used in the phase separation process [14, 15].

Concerning nonporous membranes, these are categorized as dense ceramic electrolytes such as yttria-stabilized zirconia (YSZ) and perovskite membranes [16], which allow only the permeation of ionic oxygen. Permeation through metal membranes such as palladium and a palladium alloy is based on the selective dissolution of hydrogen and diffusion through the metal membrane.

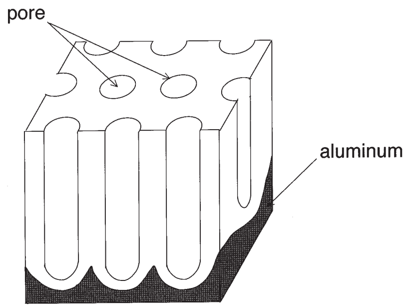

Figure 4. Pore structure of an anodic oxide aluminum membrane.

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3. LIQUID PHASE SEPARATION

3.1 Introduction

Membrane performance for liquid phase separation can be evaluated by two parameters: permeability (L_p) and rejection (R). The permeability dimension is $m^3m^{-2}s^{-1}Pa^{-1}$ in SI unit, and indicates how much solvent, such as water, permeates through the unit membrane area per second under a pressure difference of 1 Pa. Rejection, R, is the ratio of the concentration retained in feed stream over the feed concentration as defined in the following equation with the concentration of permeate, C_p, and feed, C_f.

$$R = 1 - C_p/C_f$$

R=0 indicates that no separation between the feed and permeate, while only solvent permeates with no permeation of solutes for the case of R = 1. Rejection is largely determined by the pore size and the pore size distribution. The pore size distribution of porous membranes must be sharp for selective separation. Therefore, it is important to understand the current status between pore size and inorganic materials for filtration materials. Figure 5 shows a schematic diagram of pore sizes obtained by several materials which have been used for liquid phase separation. α-alumina, which is a common material used for the preparation of a porous ceramic membrane, has excellent stability in acidic as well as basic pHs. However, there is a limitation in pore size, which is in a range of microfiltration (larger than 100 nm). On the other hand, γ-alumina, which is prepared by coating boehmite sols and sub-

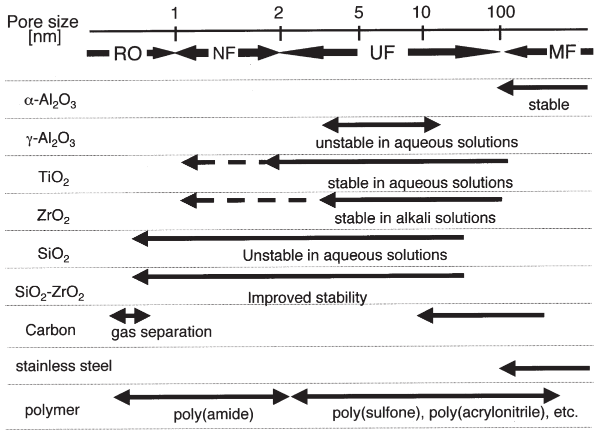

Figure 5. Materials and pore sizes for use in liquid phase separation.

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Table 4. Membrane Preparation and Filtration Performances

Preparation Methods	Material	Separation System	MWCO/ (R_{obs}/pore size)	Lpx10^{11} [$m^3m^{-2}s^{-1}Pa^{-1}$]	Ref.
Sol-gel	γAl_2O_3	PEG	≈1000	0.39	18, 19
	γAl_2O_3	Saccharose, yellow acid, direct red	400 ~ 500	0.3 ~ 0.5	23
	γAl_2O_3	Saccharose, organic electrolytes	400, 600	0.3–0.6	22, 52
	γAl_2O_3	PEG	600	0.68	28
	γAl_2O_3	PEG	900	1.3	21
	γAl_2O_3	Hexane	—	0.83	43
	γAl_2O_3	Oil (MW660)/ hexane	$R_{obs} = 0.26$	0.106	43
	TiO_2	PEG	1,000	1.7	28
	TiO_2	PEG, dyeing wastewater	1,000	3.6	27
	TiO_2	PEG 200	$R_{obs} = 0.2 \sim 1$	—	25
	TiO_2	Direct Red (MW991), Orange G (MW452); NaCl, Na_2SO_4	<1000	33.8 (PWF)	30
	TiO_2	PEG; NaCl, Na_2SO_4	500	5.5 (PWF)	29
	TiO_2	Sugars	500, 800, >1000	0.2, 2, 3.5	26
	ZrO_2, Mg doped ZrO_2	Saccharose	$R_{obs} = 0.25 \sim 0.55$	3.4	32
	ZrO_2	Direct Red (MW991), Orange G (MW452); NaCl, Na_2SO_4	<1000	22.2 (PWF)	30
	ZrO_2	Soybean oil/hexane	$R_{obs} = 0.37$		33
	HfO_2	PEG	420	0.67	38
	SiO_2-ZrO_2 (7/3)	NaCl	$R_{obs} = 0.9$	0.0066	34
	SiO_2-ZrO_2 (9/1)	Sugars	200-1,000	0.15–1.5	35
	TiO_2-$ZnAl_2O_4$	PEG, electrolytes	$d_p = 6$ nm	0.14	40
	SnO_2	Electrolytes	$d_p = 3.0$ nm	13	39
Zeolite	NaA	Water		0.0025	45
		Water/EtoH (80/20)	$R_{obs} = 0.4$	0.001	45
Anodic oxidation	Amorphous Al_2O_3	Dextran	$d_p = 20$–30 nm		12
Clay	Montmorillonite	Dextran	MWCO > 10 k	0.0046	48
	Sepiolite	PEG/PEO	300 k	1.6	49
Phase separation/ leaching	SiO_2, modified SiO_2	Water, heptane, benzene, methanol	$d_p = 4$–100 nm		73
	SiO_2-Al_2O_3		50 nm~		41

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Table 4. Continued

Preparation Methods	Material	Separation System	MWCO/ (R_{obs}/pore size)	Lpx10^{11} [$m^3m^{-2}s^{-1}Pa^{-1}$]	Ref.
Organic/ inorganic	Nafion on TiO_2	PEG, electrolyte	600	0.53	28
	Nafion on TiO_2	Supercritical CO_2	600	—	77
	Silane coupling $+\gamma Al_2O_3$	Hexane	—	0.058	43
	Silane coupling $+\gamma Al_2O_3$	Oil (MW660)/ hexane	$R_{obs} = 0.42$	0.0083	43
Dynamic	ZrO_2	Dextran	60 k	10	51
	ZrO_2	Dextran	$>$100 k	4.9	50

sequent heat-treatment, is reported to have a pore size in a range of ultrafiltration membranes (the pore size can be controlled down to approximately 4 nm), but is not as stable as in the case of α-alumina. Titania and zirconia have an excellent stability in aqueous solutions, and the pore size in the NF range is under development. Amorphous silica, which is mainly prepared via the hydrolysis and condensation of TEOS, has a great advantage in controllability of the pore size in a wide range from RO/NF to UF, but is not stable in aqueous solutions. Therefore, the incorporation of other metal oxides such as zirconia into silica has been investigated. Carbon has excellent stability in aqueous solution in acidic and alkali pH, and therefore, has potential for use as materials for filtration. Carbon membranes which have been commercialized are in a range of mainly MF and partly UF. Concerning polymeric membranes, materials for MF and UF are polyacrylonitrile, polysulfone, cellulose, and cellulose triacetate, which can be used at relatively high temperature s (≈ 80°C). For the case of polymeric RO and NF membranes, which have pore sizes of less than 2 nm, have been manufactured mostly from poly(amide). Polyamide can be controlled to give pore size less than 2 nm, but the utilization is limited normally in the pH range from 3 to 11 and at temperatures from 20 to 40°C [17].

In summary, inorganic micro- and ultrafiltration membranes have now been commercialized from α-alumina, titania, zirconia and carbon, and applied to a variety of applications. Extensive investigation has been devoted to the development of porous membranes having pore sizes in the nanofiltration range, as shown in Table 4. New trends in membrane development are summarized below, followed by reviewing practical applications.

3.2 Sol-Gel Membranes

In the sol-gel process, porous ceramic membranes are manufactured by sol-coating on porous substrates, and drying for gelling, followed by firing process.

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The pore sizes of porous membranes by the sol-gel process can be controlled by colloidal diameters and firing temperature, since the pores are considered to be formed as spaces among packed colloidal particles, i. e., interparticle pores.

3.2.1 Alumina Membranes

Alumina porous membranes have been prepared by the Yoldas method. That is, boehmite sol is prepared by the hydrolysis of aluminum butoxide or aluminum propoxide in hot water (higher than 80°C), followed by peptization by acids such as nitric acid [18, 19]. γ-alumina membranes can be obtained after firing boehmite membranes at 400–600°C. Figure 6 shows a schematic representation of γ-alumina membranes [19], indicating that plate-shaped particles (boehmite and γ-alumina after firing) are packed to form slit-shape pores, in which distance between the slits is approximately several nms. Figure 7 shows molecular weight-cut-off curves, that is, the rejection of various molecules plotted as a function of molecular weight [18–20]. The molecular weight cut-offs (MWCO), which are defined as a molecular weight showing a rejection of 90%, are in the approximate range of 2,000 to 10,000, depending on the firing temperature. MWCO fired at higher temperature increases because of the growth in particle size. A further increase in firing temperature above 1000°C causes a phase transition of γ-alumina to α-alumina, resulting in the conversion of the UF membranes to MF membranes. Schaep et al. [21] prepared a γ-alumina membrane having MWCO of 900 by firing at 400°C, and confirmed that the higher firing temperature resulted in the larger MWCOs. On the other hand, Larbot et al. [22] reported the successful preparation of colloidal sol solutions which gave a pore size of 0.6 nm after firing at 450°C. γ-alumina membranes having MWCO of 350 and 450 were prepared by firing at 400°C and 650°C, respectively. As mention above, γ-alumina is not stable, especially in aqueous solution, which was confirmed by dynamic filtration test for solutions of pH2 [21]. At present, no γ-alumina membranes have been commercialized. Another approach to utilize γ-alumina is to apply it to nonaqueous solutions. Persin et al. [23] applied γ-alumina membranes fired at 450°C (MWCO ≈ 400) to toluene/cyclohexane separation in pervaporation and reported a separation fac-

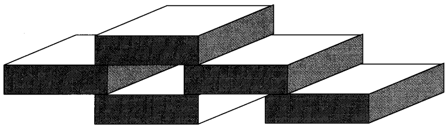

Figure 6. Pore structure of γ-alumina (boehmite) membrane proposed by Leenaars and Burggraaf [19].

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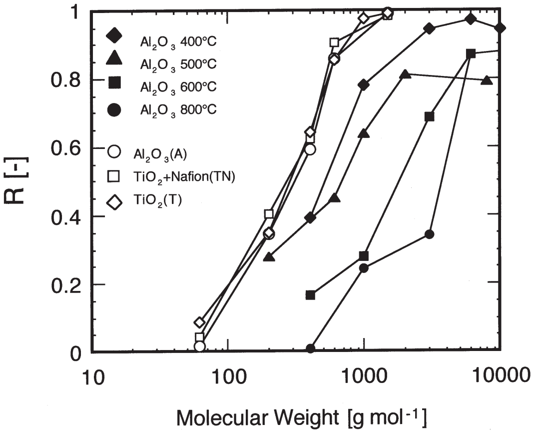

Figure 7. Molecular cut-off curves for alumina and titania porous membranes. Al_2O_3 membranes (filled symbols) were fired at temperatures of 400, 500, 600 and 800°C [20, 23, 28].

tor of 3 for toluene over cyclohexane. No separation occurred through γ-alumina membranes fired at 650°C.

3.2.2 Titania Membranes

Titania membranes show excellent chemical resistance, and can be used in both acidic and basic pHs; and moreover, they show interesting photocatalytic activity. Titania ultrafiltration membranes have been commercialized by several companies. At present, extensive efforts have focused on the preparation of porous membranes having small pore sizes in the NF range (1 ∼ 2 nm). Since pore sizes are believed to be controlled by the seizes of the packed particles, controlling the sol size is a crucial process for membrane processing. Anderson et al. [24] prepared nano-sized TiO_2 and ZrO_2 particles (3 ∼ 5 nm) by carrying out hydrolysis and condensation reactions of metal *tert*-amyloxide with a small amount of water (molar ratio of $H_2O/Ti = 3{\sim}5$) in *tert*-amyl alcohol solutions. Hydrolysis and condensation reactions of metal alkoxides are written as follows.

$$Ti(OR)_4 + H_2O \rightarrow Ti(OR)_3(OH) + ROH \quad \text{(hydrolysis)}$$

$$Ti(OR)_4 + Ti(OR)_3(OH) \rightarrow (RO)_3TiOTi(OR)_3 + ROH \quad \text{(condensation)}$$

Since both reactions take place by nucleophilic substitution, the electronegativity and the size of alkoxy groups is important. By using a large branched alkoxy group (*tert*-amyl alkoxide), the reaction rate can be reduced, resulting in

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small-sized sols. An amorphous phase predominated in the xerogel dried at room temperature and fired at 300°C, and phase transition from amorphous to anatase and from anatase to rutile occurred at from 300∼400°C and 400 ∼ 600°C, respectively. Therefore, it is important to control firing temperature in order to obtain controlled pore sizes of membranes. Titania membranes which were coated on porous alumina membranes and fired at 200°C, showed approximately a 100 % rejection of polyethylene glycol 200 (PEG200, M. W. 200), depending on operating conditions [25]. Another strategy for controlling MWCOs is the appropriate choice of sol diameters, which is used at the final coating for the separation top layer. Tsuru et al. [26] successfully prepared a variety of MWCOs for TiO_2 membranes at the same firing temperature of 450°C using sol solutions having different sizes of sol diameters, as shown in Fig. 8. M1, M2, and M3 show MWCOs approximately 500, 600, and 800, while M4 shows nearly no rejection for α-dextrin (MW 972).

On the other hand, Société des Céramiques Tehniques (SCT) claimed that they had commercialized TiO_2 NF membranes having a MWCO of 1,000 [27, 28] based on research work by Commissariat à l'Energie Atomique (CEA). Colloidal sols with a diameter of 15 nm, which showed an anatase phase and which were stable upto 600°C, were coated on porous alumina supports and fired at 500°C. The molecular weigh cut-off curves of titania (T), alumina (A), and titania-nafion composite (TN) membranes prepared by this research group are also shown in Fig. 7 [28]. Voigt et al. [29] prepared polymeric sols from a solution of Ti-isoproxide in isopropyl alcohol by the addition of a small amount of water. NF membranes, which were prepared by coating the polymeric sols on a TiO_2 intermediate layer (pore size 5 nm, prepared by colloidal TiO_2 sols), followed by firing at 450°C, had a MWCO of 480 and a pure water flux of 20 l/(m^2 h bar), and were

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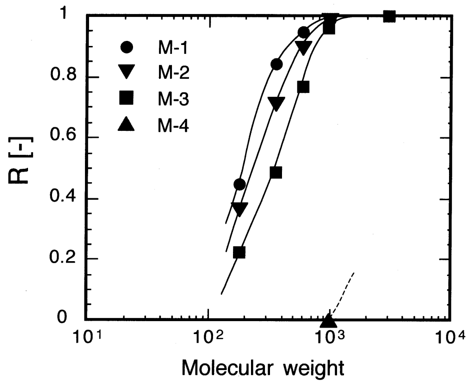

Figure 8. Molecular weight cut-off curves for titania porous membranes (solutes: sugars, 500 ppm) [26].

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applied to the separation of electrolytes. Benfer et al. [30] also developed TiO_2 NF membranes by the polymeric sol route. Tetraethyl orthotitanate was partially hydrolyzed at conditions where the molar ratio of water over the alkoxide was less than 1, followed by the addition of an acid or organic base to control the viscosity of the polymeric sol solution, i.e., the size of the polymeric network. They also prepared zirconia porous membranes by the same method. Filtration performance of TiO_2 membranes, as summarized in Table 4, shows comparable water permeabilities to those of polymeric NF membranes [17].

3.2.3 Zirconia Membranes

Zirconia, which is stable as well as titania, especially, in alkali solution, is also one of the promising materials for separation membranes. Chemical stability of porous yttria-doped zirconia microfiltration membranes was evaluated at room temperature and 80°C in aqueous solutions of acids ($pH \approx 2$) and bases ($pH \approx 12$) [31]. Dissolution of yttria was detected in acid solutions during a experimental period of more than 30 days, while no dissolution of yttria and zirconium was detected in basic solutions. Several manufacturers have commercialized zirconia UF membranes, but not NF membranes. Zirconium propoxide [32] or butoxide [33], which are mainly used as precursors of zirconia sols, are highly sensitive to water to form suspensions (the reaction rate with water is much faster than titanium alkoxide), the preparation of nano-sized sols is difficult. Therefore, very few reports have appeared on the successful preparation of zirconia nanofiltration membranes. Vacassy et al. [32]added acetylacetone to zirconia propoxide to prevent hydrolysis, and reported a successful preparation of porous zirconia membranes showing a water permeability of 3.4×10^{-11} m s^{-1} Pa^{-1} and a rejection of 55% towards saccharose (MW=342).

3.2.4 Composite Oxide Membranes

Amorphous silica, which is an acidic metal oxide, is not stable in aqueous solutions, especially in neutral and alkaline pHs, but has a great advantage in terms of pore-size controllability. Therefore, the incorporation of zirconia into silica has been investigated. TEOS and zirconium propoxide or zirconium butoxide were applied to the composite precursor for reverse osmosis membranes [34] and nanofiltration membranes [35, 36]. As shown in Fig. 9, the MWCOs of silica-zirconia membranes (molar ratio: 9 Si–1 Zr), were controlled in a range from $200 \sim 1{,}000$, showing a smaller MWCO compared with those of γ-alumina and titania. Tsuru et al. applied silica-zirconia NF membranes to separation in aqueous solutions [35, 36], and nonaqueous solutions [37]. It should be noted that the stability in aqueous solutions was improved by incorporation of zirconia into silica [34, 35].

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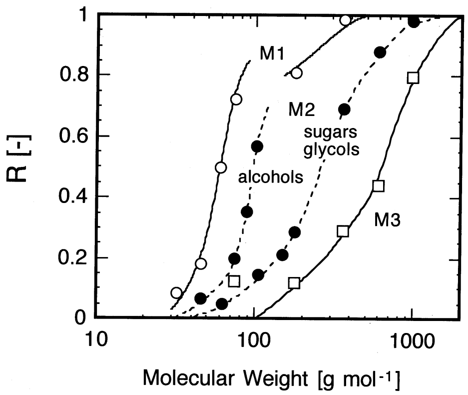

Figure 9. Molecular weigh cut-off curves for silica-zirconia porous membranes (solutes: sugars, 500 ppm) [35].

3.2.5 Other Materials

Hafinia, which can be sintered up to 1850°C without transition of the monoclinic form, was used for preparing nanofiltration membranes, showing a MWCO of 420 and a pore size near 1 nm by sintering at 450°C [38]. Various types of metal oxides such as SnO_2 [39], $ZnAl_2O_4$ [40], which were prepared by the sol-gel process for expecting different surface chemistry from TiO_2 and ZrO_2, have been proposed for the fabrication of porous membranes, although the pore size is in the UF range.

3.3 Other Preparation Processes

Nakashima et al. [41] developed tubular glass membranes of different compositions from a so-called Vycor composition, by a phase separation/ leaching method of $CaO—Al_2O_3—B_2O_3—SiO_2$ glass. The pore sizes, which were controlled in a range larger than 50 nm, showed a sharp distribution. The glass membranes were used for filtration in aqueous solutions. Another interesting application is membrane emulsification by taking advantage of the sharp pore size distribution.

Carbon, which has stability in aqueous as well as nonaqueous solutions, is also a candidate for porous inorganic membranes. At present, a few manufacturers have commercialized carbon UF membranes, the pore sizes of which are larger than 10 nm. No carbon nanofiltration membranes have been reported, while carbon gas separation membranes, which have pore sizes less than 1 nm, have been reported by several groups [7]. Nomura et al. [42] coated poly(vynilydene chlo-

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ride) on α-alumina supports and pyrolyzed them at 825°C in a N_2 atmosphere. The porous carbon membranes consisted of two types of pores: mesopores of 10 nm (interparticle) and micropores of 0.7 nm (intraparticle), showing a MWCO of 10,000 and a adsorption ability based on the micropores.

Organic-inorganic composite membranes have been investigated for their excellent stability by inorganic materials and high selectivity of organic membranes. Nafion, which is a negatively charged polyelectrolyte membrane, was used for a composite membrane with a mesoporous titania membrane [28]. γ-alumina membranes were modified with silane coupling agents to reduce the pore size and enhance the selectivity of toluene over a toluene/ lubricant mixture [43]. Ohya et al. [44] modified the pores of α-alumina membranes by the molecular-wise growth in liquid and gas-phase co-polymerization of polyimide to control pores sizes for UF and gas separation membranes.

Several types of zeolite membranes such as A-type, Y type, silicalite, ZSM-5 etc. have been developed, and have been applied mainly to gas and pervaporation separations. Kumakiri et al. [45] prepared A-type zeolite membranes by hydrothermal synthesis with seed growth, and applied these to the reverse osmosis separation of water/ ethanol mixtures. The zeolite A membrane showed a rejection of 40 % and a permeate flux of 0.06 $kgm^{-2}\ h^{-1}$ for 10 wt% ethanol at a pressure difference of1.5 MPa, while a permeate flux of 0.8 $kg\ m^{-2}\ h^{-1}$ and a separation factor of 80 were obtained in PV.

One of the features of inorganic membranes is their controlled pore structure. Anodic aluminum oxide membranes have uniform cylindrical pores, and were applied to an investigation of the analysis of transport mechanism [12]. Another route involves the application of a micelle template to membrane preparation [46]. Cubic mesoporous silica (MCM48) membranes were prepared on a stainless steel supports [47] to possible applications for filtration membranes and membrane reactions.

Porous membranes were prepared by using clays such as montmorillonite [48] and sepiolite [49], and the dynamic filtration of solutions having fine particles of hydrous zirconium oxide [50, 51], although their pore sizes are in a range of ultrafiltration membranes.

3.4 Applications

Inorganic microfiltration and ultrafiltration membranes have been used in a wide variety of processings. Typical applications were reported in detail by Hsieh [2] and Bhave [3], and are summarized in Table 5. Microfiltration, which has pore sizes larger than 100 nm, can be applied to remove or concentrate particles or microorganisms, while ultrafiltration membranes have been used for the separation of components, the sizes of which are from 2 to 100nm, such as proteins and colloidal solutes. In this section, potential applications will be reviewed.

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Table 5. Applications of Liquid Phase Separations

Application Area	Application Examples
Water treatment	Drinking water, wastewater treatment
Waste oil treatment	Oil-water separation, purification of used oils
Dairy industry	Bacteria removal of milk, concentration of milk, concentration of protein
Beverage	Clarification of fruit juice, clarification of wine, bacteria removal, microorganism separation from fermented
Biotechnology	Microorganism separation and cell debris filtration, plasma separation
Petrochemical processing	Removal of precipitated heavy metals and solids

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3.4.1 Water Treatment

One of the largest applications is water treatment, including drinking water as well as wastewater. For the case of water treatment using porous membranes, the surface charge can play a very important role in determining ion separation and flux based on electrokinetic effects. The surface charge of a membrane influences membrane performance in several ways, as depicted in Fig. 10. Ion separa-

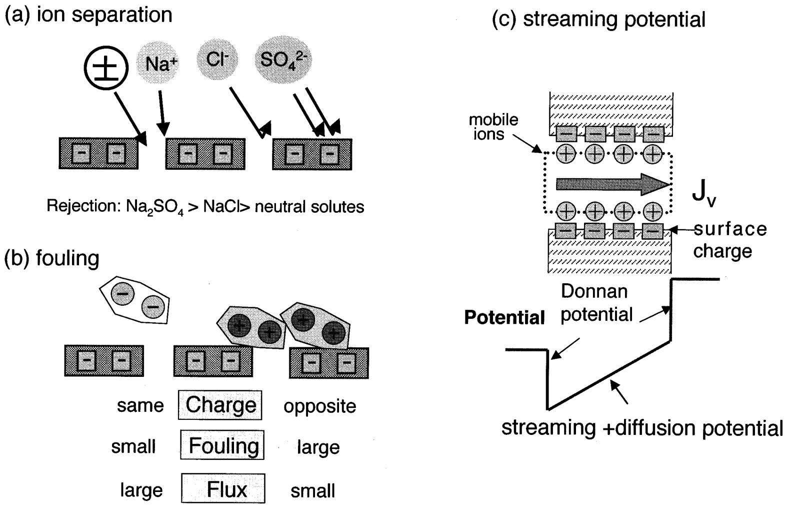

Figure 10. Effect of surface charge on membrane performance. (a) ion separation, (b) fouling, and (c) streaming potential.

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tion is possible based on electrostatic interaction between ions and surface charge; coions, which have the same charge as the membrane surface, receive repulsive force from the membrane surface, which is referred to Donnan exclusion. The repulsive force for divalent coions is greater than for monovalent coions, and, therefore, ion separation can be successfully carried out using nanofiltration membranes, the pore size of which is even much greater than ion sizes [52–56]. Transport mechanism through charged porous membranes in filtration, where electric migration, diffusion and convection occurs simultaneously, has been investigated by assuming that a membrane consists of a homogeneous gel [55], a bundle of capillary [57], or granular pores [58]. Figure 11 shows the separation of a $Ni(NO_3)_2/HNO_3$ mixture using a silica-zirconia membrane [52]. At low pH $(\mathrm{pH} = 1 \sim 3)$ where the surface is positively charged, the nickel ions were strongly repelled (rejection is large), while hydrogen ion was concentrated in the permeate (negative rejection) so as to maintain electroneutrality with the permeation of nitric ion (counterion to the membrane surface charge.) It should be noted that these phenomena were theoretically predicted. For the case of particles such as silica, kaolin etc. and macromolecules such as proteins, the electric force between a membrane and the solutes whose charge is opposite that of a membrane, leads to membrane fouling, resulting in a decrease in permeation flux through the membranes, as shown in Fig. 10 (b). Therefore, the fouling problem can be possibly solved or reduced by controlling the surface charge (polarity, density, etc.) of the membrane. In addition, permeate volume flux is affected by the presence of inorganic electrolytes, the size of which are approximately from 0.2 to 0.4 nm. For the case of negatively charged membranes in which the concentration of cation is greater than that of anion, a streaming potential is generated to reduce the flux of cation and accelerate that of anions, so as to maintain a no-electric current condi-

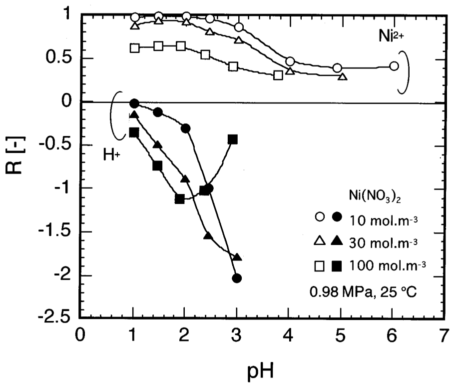

Figure 11. Rejection of nickel nitrate and nitric acid as a function of pH of feed solution. Feed concentration of nickel was kept at 10, 30, and 100 mol $m^{-3.}$

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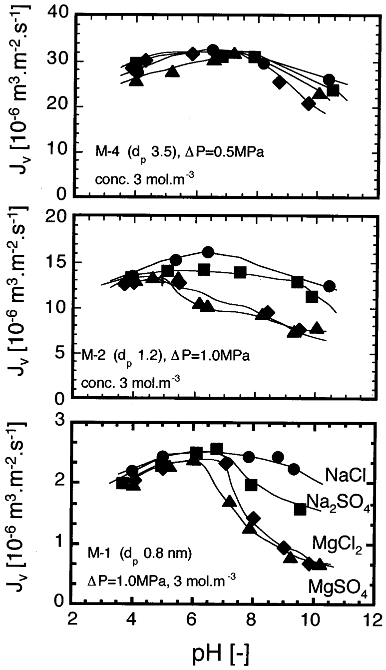

Figure 12. Effect of pH on flux for membranes of different pore size M-1 (d_K=0.8nm), M-2 (d_K=1.2nm), and M-4 (d_K=3.5nm) [26].

tion through the membrane under filtration conditions. As a whole, the electrical potential force acting on the fluid in the membrane pore, which has an excess amount of positive charge in the form of mobile ions, is generated toward the feed stream, which reduces the effective force for the permeation of liquid. The permeate volume flux of charged membranes is smaller than that of neutral membranes which have the same pore structures, and this effect is called an "electroviscous effect." [59–62]. From an experimental point of view, the effect of surface charge has been investigated using microfiltration and ultrafiltration membranes, most of which are prepared from α-alumina. Permeate flux has been reported to show the maximal flux at the iso-electric point (IEP), since the electroviscous effect can be neglected because of no surface charge. Recently, the effect of counterions on porous titania membranes which had a MWCO in the nanofiltration range, was reported [26], as shown in Fig. 12. Maximal volume flux was observed for the three membranes at the IEP of approximately pH 6 ~7. At pH values lower than the IEP, permeate flux was approximately the same, irrespective of the type of electrolyte. The permeate volume flux decreased drastically for $MgCl_2$ and

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$MgSO_4$, and the ratio of flux reduction appears to be pronounced for membranes having small pores; the permeate flux of $MgCl_2$ and $MgSO_4$ at pH 9 was approximately 50 % and 25 % compared with that of NaCl at pH9 for M-2 and M-1, respectively. It has been suggested that adsorbed divalent counterions (Mg^{2+}) reduced the effective pore sizes and hydrodynamically resisted the permeation through nano-sized pores.

In terms of practical applications, fouling, which occurs via formation of a cake/gel layer on the membrane surface and pore blocking by colloidal particulates and adsorption of dissolved solutes, reduces permeate flux during filtration, and is an important problem to be solved. Modification of membrane surface with a helix geometry configuration, which promoted turbulence, was found to be effective in recovering permeate flux by a factor of 6, compared with non-modified membranes [63].

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3.4.2 Application for Nonaqueous Systems

Membranes have been developed for applications in aqueous systems such as desalination and drinking water treatment. Recently, it has been expected that membrane separation will be expanded to various applications such as separation of non-aqueous solutions and filtration in non-aqueous solutions. Table 6 summarizes applications of RO, NF, UF and MF in non-aqueous systems. It should be noted that nonaqueous separation is also under development in pervaporation using zeolite membranes. Several attempts have been made to separate/purify organic solvents using polymeric membranes. Iwama and Kazuse [64] developed polymeric ultrafiltration membranes which were made from polyimide, and applied these to the removal of large molecules from various solvents. Ohya et al. [65] separated gasoline and kerosene by means of polyimide membranes. Other applications involve the purification of solvents [66], and the separation and/ or concentration of macromolecules in organic solvents, such as fatty acids in solvent extracts [67]. Lencki and Williams [68] reported on the effect of aqueous methanol, ethanol and acetonitrile solutions on the flux behavior of cellulose and polysulfone ultrafiltration membranes. The swelling of polymeric materials by organic solvents caused changes in the pore structures of the membranes, and eventually disrupted their integrity. Recent papers [69, 70] reported the performances of solvent-resistant polymeric membranes, although the experimental conditions (types of solvents, temperature) remain limited.

As mentioned above, a major advantage of ceramic porous membranes is their resistance to organic solvents. Petrochemical processing is one of the applications to which organic membranes cannot be applied. Ceramic membranes: ZrO_2/C (pore size 140 $\sim$ 3.7 nm), silica (10 nm), and γ-alumina (5nm) mem-

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Table 6. Summary of RO/NF/UF for Non-aqueous Systems

Method	Feed	Membranes	Notes	Ref.
Organic membranes				
UF	Reuse of used organic solvents	Poly(imide)	MWCO2,000~	64
UF	Permeation of aqueous ethanol	Commercial UF (PS (PTGC, PTTK), CA (PLGC, PLTK); MWCO 10, 30kDa)	Permeability changed because of swelling	68
NF	Recycle of aqueous ethanol solution without changing compositions	Commercial NF (YM2, YC05, NTR759), CA	MWCO decreases with ethanol concentration	66
NF/RO	Fractionation of hydrocarbon in toluene separation of gasoline and kerosene	Poly(imide)	$L_p = 1.5 \times 10^{-13}$, MWCO = 170–400; $\alpha = 19$ ($\Delta P = 10$ MPa, 423 K)	65
RO/NF	Permeation of alcohols, paraffin, ketones, acetates, water; binary mixtures	MPF-50, 60 (silicone)	Nonlinear dependency of flux on composition, surface tensiton is important; no separation for solvent mixtures	69
RO/NF	Solutes: safranin, brilliant blue, vitamin B12; solvents: water, methanol	MPF-44, 50, 60	Membrane performance showed time-dependence	70
NF/RO	Separation of hydrocarbon and fatty acid from ethanol and hexane solutions	Cellulose triacetate		67
Inorganic membranes				
UF/NF	Removal of oil (MW 600) from hexane solution	γ-Al_2O_3, modified γ-Al_2O_3	$L_p = 5.8 \times 10^{-13}$ (Hexane), $R_{obs} = 0.4$	43
UF	Removal of asphaltene from crude oil	ZrO_2, SiO_2, γ-Al_2O_3		71

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Table 6. Continued

Method	Feed	Membranes	Notes	Ref.
UF	Treatment of waste lubricating oil	ZrO_2 (50 nm), SiO_2 (10, 5), γ-Al_2O_3 (5)		72
NF	Super critical CO_2	TiO_2		76
UF	Soybean oil/hexane (37/63 wt %)	Anodisc (Whatman, 20 nm)	Rejection = 0.2	70
NF	PEG/Ethanol	SiO_2-ZrO_2	MWCO 300, 600, 1000, >1000; stable	77

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branes were applied for an oil deasphalting process at temperatures in the range of 115 ~ 180°C [71]. ZrO_2/Carbon membrane showed the best results, while no permeation occurred through silica and γ-alumina membranes which had a strong affinity for the feed solution. ZrO_2, silica and γ-alumina membranes were applied for cleaning up used oils at temperatures from 150–260°C. A γ-alumina membrane showed a gradual decrease in flux as a result of fouling, which was caused by affinity between components in the feed and the membrane surface, while the other two membranes showed a steady flux. The treated oils, which were separated from heavy metals, ash, and suspended solids, are reported to be considered as clean oils [72].

Affinity between feed solutions with the membrane surface plays an important role in determining permeation properties through porous membranes. The effects of pore sizes on permeation performances through porous membranes were investigated based on the dependency of the types of solvents and temperature [73, 74]. It has been made clear that the transport mechanism through inorganic porous membranes in the NF range is an activated process and does not obey the viscous flow mechanism which is an ordinal flow mechanism through UF and MF membranes having relatively large pore sizes. Another interesting application is the use of inorganic membranes for separation and concentration in nonaqueous solutions such as toluene, ethanol, and hexane [37, 43, 75] and in supercritical fluids [76]. Silica-zirconia membranes having pore sizes in a range of 1–4 nm showed molecular weight cut-offs in methanol solutions at 300, 600, 1000, and >1000, as shown in Fig. 13, and the stability in nonaqueous solutions was confirmed [37]. It should be noted that pore sizes were evaluated by nanopermporometry [77], which had been described as permporometry [1, 78] or dynamic flow-weighted porometry [79]. This relatively new technique is based on the capillary condensation of vapor and the blocking effect of permeation of a non-condensable gas, and quite effective to characterize a pore size distribution active for separation in a range from 0.5 to 30 nm [77].

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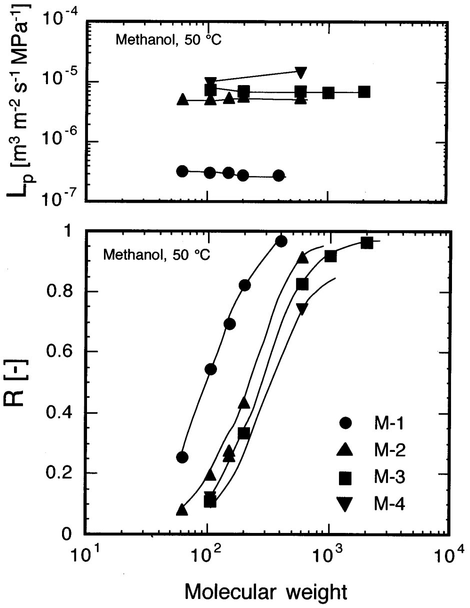

Figure 13. Volume flux and rejection as a function of molecular weights of solutes methanol solution, 50˚C, 500 ppm; applied pressure for membrane M-1, M-2, M-3 and M-4 was 3.0, 2.0, 1.0, and 2 MPa, respectively).

3.4.3 Photocatalytic Activity

Photo-catalytic reactions by titania (TiO_2) have drawn a great deal of attention because of its ability to catalyze the decomposition of various types of aqueous pollutants. The principles of photocatalytic reactions for the degradation of toxic organic pollutants are based on the photogeneration of OH radicals by positive photoholes, which are induced by ultraviolet irradiation, and the subsequent oxidative decomposition of organic pollutants. Photocatalytic reactions have been extensively investigated using either batch discontinuous reactors, in which the catalyst is suspended in solutions, or continuous fluidized-bed reactors. A new type of photocatalytic reaction system in which the titania itself is immobilized as a porous membrane capable of not only filtration but also photocatalytic reaction, was proposed [80]. As shown in Fig. 14(a), purified water can be obtained in the permeate stream, since the pollutants are decomposed while permeating through the porous TiO_2 membranes. In addition, Fig. 14(b) shows another possible advantage of porous TiO_2 membranes, in that membrane fouling can be reduced by photodegradation of organic foulants and the permeating volume flux can be increased [81].

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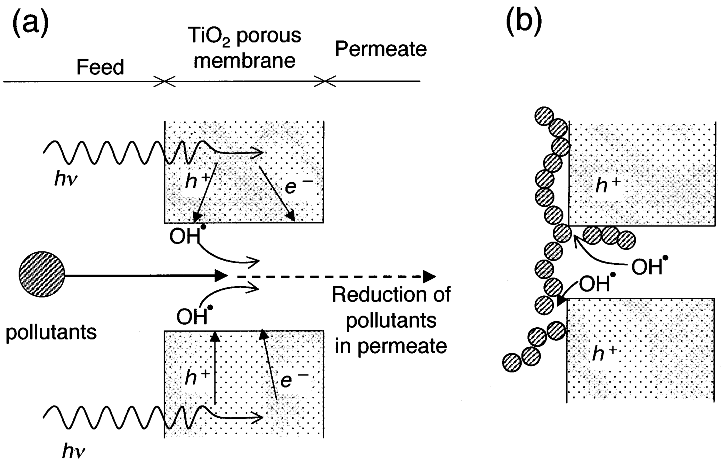

Figure 14. Schematic concept of photocatalytic reaction in a filtration system. (a) Organic pollutants are decomposed while permeating TiO_2 pores; (b) foulants on the surface of TiO_2 membranes are decomposed, and permeating volume flux is increased [78].

Figure 15 shows a time course for the trichloroethylene (TCE) concentration in the feed and permeate streams using a porous TiO_2 membrane having a MWCO of 30,000 [80]. When UV light (wavelength 350 nm) was applied onto the TiO_2 membrane, the concentration in the permeate stream decreased stepwise by approximately 5 ppm. The reduction of 5 ppm in permeate concentration was maintained during the course of UV irradiation. After switching off the lamp, the

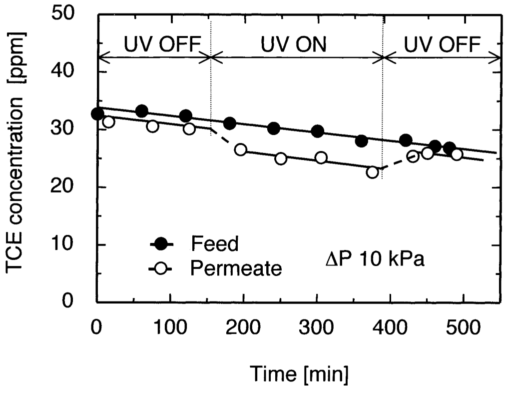

Figure 15. Trichloroethylene concentration as a function of elapsed time (ΔP≈10 kPa, MWCO≈30,000).

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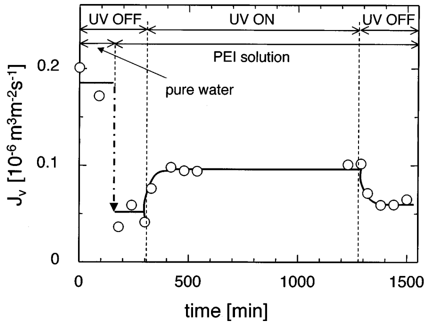

Figure 16. Permeate flux, J_v, as a function of elapsed time. The experimental sequence was as follows; (pure water, UV off) → (PEI, UV off) → (PEI, UV on) → (PEI, UV off). PEI concentration 100 ppm, AP=20 kPa, pH 10.5, MWCO≈500.

permeate concentration increased nearly to a level equal to the feed concentration. Figure 16 [80] shows another application of photocatalytic activity using polyethyleneimine (PEI) as a foulant. The volume flux of PEI solutions of 500 ppm decreased drastically to 0.05×10^{-6} $m^3m^{-2}s^{-1}$ from that of pure water of 0.2×10^{-6} $m^3m^{-2}s^{-1}$, because of fouling of the TiO_2 membrane by PEI. The volume flux increased stepwise to 0.1×10^{-6} $m^3m^{-2}s^{-1}$ as the result of UV irradiation, and was maintained as long as 1000 min during the period of UV irradiation. After switching off the UV lamps, the volume flux decreased to approximately the same level of the volume flux before UV irradiation. Both figures confirm the concept of photocatalytic reactions in a filtration system in which filtration and a photocatalytic reaction occur simultaneously.

4. CONCLUDING REMARKS

Porous ceramic membranes have been reviewed from the viewpoint of membrane preparation methods and applications for use in liquid phase separation. These new classes of porous ceramic membranes hold considerable promise in applications such as separation in nonaqueous systems, separation at high temperatures, and photocatalytic activity. The preparation of porous ceramic membranes, which need to have uniform pore sizes, to be as thin as possible without defects, seems to represent a different strategy from conventional preparation of ceramic bulk bodies. Surface chemistry plays an important role in membrane performance, and further investigation is required for the transport mechanism of liquid through porous membranes. This new research field will contribute much to the development of membrane science and technology.

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