

## Pervaporation separation of ethanol via adsorbent-filled silicon rubber membranes

Ling-Yun Ji<sup>1</sup>, Bao-Li Shi<sup>\*1,2</sup> and Qing-Wen Wang<sup>2</sup>

<sup>1</sup>Department of Chemistry, College of Science, Northeast Forestry University, Harbin, 150040, China

<sup>2</sup>Key Laboratory of Bio-Based Material Science and Technology of Ministry of Education,  
Northeast Forestry University, Harbin, 150040, China

(Received May 20, 2014, Revised October 15, 2014, Accepted October 16, 2014)

**Abstract.** Pervaporation is the most promising technique for the recovery of ethanol from the fermentation system. To date, extensive research has been conducted on the exploration of membrane materials with favorable properties. In this paper, we primarily review the performance of adsorbent-filled rubbery membranes. In addition, the fundamental mechanisms of ethanol and water molecules transportation through composite membranes are demonstrated, particularly from the perspective of cluster formation. Finally, future prospects are also analyzed to develop the guidelines for the future development of excellent membrane materials for ethanol concentration. This paper is not meant to be an exhaustive overview, rather a specialized summary that allows readers to select the information appropriated to their topics.

**Keywords:** mixed matrix membranes; pervaporation; ethanol; PDMS; cluster

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### 1. Introduction

Because of the escalating demand and depleting supply of conventional resources, i.e., fossil fuels, it is imperative to develop sustainable alternative resources to alleviate humankind's reliance on the petroleum and to reduce the environmental pollution from fossil fuel combustion. The application of biomass to an energy source by the fermentation process to produce bio-ethanol has gained progressively more attention from the governments worldwide in recent years (Wei *et al.* 2014, Chen and Qiu 2010).

Traditional fermentation is an attractive technique for the production of ethanol directly. However, it is known that the process is seriously inhibited by ethanol itself. As a consequence, rather low ethanol concentration is obtained in the final fermentation broth. One approach to relieve such negative impact on the productivity of ethanol is to remove ethanol from the fermentation broth consecutively. Until now, methods combined into a fermentation system with a continuous mode include vacuum distillation, solvent extraction, gas stripping, and membrane pervaporation. Among them, pervaporation has been only used on a pilot scale and is not commercially viable for this application, while the other technologies are practicable. However, membrane pervaporation integrated with a bioreactor plays a dominant part in realizing the continuous fermentation because of its energy-saving, cost-effective, and environmentally friendly

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\*Corresponding author, Ph.D., E-mail: [shi\\_baoli@yahoo.com](mailto:shi_baoli@yahoo.com)

qualities as well as the fact that it has no negative influence on the microorganisms (Abdehagh *et al.* 2014, Van der Bruggen and Luis 2014, Lipnizki 2010).

Pervaporation is a separation technique involving a non-porous organic or nanoporous inorganic membrane for the separation of various components from solutions and liquid mixtures (Li *et al.* 2010). The process is, in principle, based on the difference in the permeation rates of components. Commonly, a liquid mixture is partially vaporized during transporting through a membrane by means of a vacuum at the downstream side. Then the vapor is condensed in a collector when the temperature decreases. In general, three classic groups exist, depending on the feed type and purpose of separation: hydrophobic, hydrophilic, and target organophilic pervaporation (Dobrak *et al.* 2010). Thereinto, pervaporation with hydrophobic membranes could be of potential use in industry, because the method would be easy and economical when applied in the recovery of volatile organic solvents, the removal of alcohol from alcoholic beverages, or the recovery of aroma compounds from fruit juices (Vankelecom *et al.* 1997a). At the same time, hydrophilic pervaporation, which involves either dehydration of organic compounds or water extraction from mixture, is the most studied field (Khajavi *et al.* 2009). The separation of organic compound mixtures, such as methanol/methyl-tert-butyl ether (MTBE), usually relies on the target organophilic membrane unit operation.

Membrane is the key element in the pervaporation process, and its performance for the recovery of ethanol from ethanol dilute solution is primarily assessed by the permeation flux  $J$  ( $\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ) and separation factor or selectivity  $\alpha$ . The flux and selectivity are respectively described by the following equation

$$J = \frac{Q}{A \cdot t} \quad (1)$$

where  $Q$  is the amount of penetrants (g),  $A$  denotes the effective membrane area ( $\text{m}^2$ ), and  $t$  is the operation time (h).

$$\alpha = \frac{Y_A \cdot X_B}{X_A \cdot Y_B} \quad (2)$$

where  $X_A$  and  $X_B$  represent the ethanol and water mass fractions in the feed solution, respectively.  $Y_A$  and  $Y_B$  represent the mass fraction of ethanol and water in the permeation, respectively. In addition, the subscripts  $A$  and  $B$  stand for ethanol and water, respectively.

Extensive research has been conducted on the exploration of optimized hydrophobic polymeric membrane materials to maximize the separation performance of ethanol permselective membranes in items of separation factor, flux, and operation stability. Although several species of hydrophobic inorganic membranes (Sommer and Melin 2005, Tin *et al.* 2011), e.g., hydrophobic zeolite membranes (Brown *et al.* 2003), ceramic membranes, and silicalite membranes (Lin *et al.* 2001), exhibit considerably excellent separation properties in dilute ethanol solution, later research indicates that the raw inorganic materials are difficult to process and expensive to fabricate (Vu *et al.* 2003a). Furthermore, the inorganic membranes are easily plagued by cracks and gaps, inherently fragile, and difficult to transform into a high-surface-area module (Vu *et al.* 2003a, Aroon *et al.* 2010).

Regarding organic membranes, non-porous poly(1-trimethylsilyl-1-propyne) (PTMSP) has already been massively employed by researchers to separate ethanol from aqueous mixtures (Cleas *et al.* 2010, 2012) because of its large free volume and hydrophobicity. The ethanol-water separation factor for PTMSP has been reported to range from 9 to 26 (Vane 2005). Despite the

good characteristics of PTMSP for the ethanol concentration, the separation factor and total flux declined prematurely with the operation time (Gonzalez-Velasco *et al.* 2002), which makes it nearly impossible to manufacture on a commercial scale. Gonzalez-Velasco *et al.* (2002) thoroughly studied how the transport properties decrease with operation during pervaporation in 10 wt% ethanol-water mixtures. In addition, polypropylene (PP) and porous polytetrafluoroethylene (PTFE) membranes have exhibited ethanol permselective properties but with mediocre performances. Ghofar and Kokugan (2004) tested new PP and PTFE membranes and compared them with the previous PV data. Consequently, it is still a common phenomenon that appropriate materials with outstanding ethanol-permselective properties are few, and their separation performance cannot meet the requirements of commercial processes at their present stage. Polydimethylsiloxane (PDMS), which is considered to be the most promising membrane material, has been intensively studied recently. The material is often referred to as “silicone rubber,” and has favorable thermal stability, solvent resistance, and chemical and physiologic inertness (Pouget *et al.* 2010). PDMS contains a siloxane (Si-O) backbone substituted with methyl groups, which has been successfully applied in various membrane techniques, such as pervaporation, gas separation (Vu *et al.* 2003b), vapor permeation, solvent-resistant nanofiltration (Vandezande *et al.* 2008), and dialysis (Nitsche *et al.* 1998, De Smet *et al.* 2003).

Because of the poor film-forming property and weak mechanical strength of the pure PDMS, a highly porous substrate is commonly used to support the thin separation layer to form a composite membrane. Generally, the separation layer of the composite membrane determines the pervaporation performance, while the porous support provides the mechanical strength (Lee *et al.* 2012). Organic polymeric supports such as poly(vinylidene fluoride) (PVDF), polyacrylonitrile (PAN), cellulose acetate (CA), poly(tetrafluoroethylene) (PTFE), polyethylene (PE), polyether sulfone (PES), polysulfone (PSf), polyamide (PA), and polyetherimide (PEI) have been estimated for the preparation of composite PDMS membranes (Li *et al.* 2004, Guo *et al.* 2010). Alternatively, the utilization of inorganic support also attracted much attention. Liu *et al.* (2012) reviewed the preparation and application of macroporous ceramic-supported polymer composite pervaporation membranes. Xiangli *et al.* (Xiangli *et al.* 2007, 2008), Wei *et al.* 2010) developed a type of PDMS/ceramic composite membrane using commercialized microporous ceramic supports. The prepared PDMS composite membranes exhibited high mechanical strength, solvent resistance, low transport resistance, and ability to be operated at higher temperatures. However, this type of membranes was easily made brittle, and the effective area was strongly limited. Consequently, it was difficult to satisfy the industrial requirements.

Unfortunately, the separation factors of the pure PDMS active layer for ethanol-water ranged from only 4.4 to 10.8, with an average of 7-8 (Vane 2005), and the fluxes were usually less than  $1000 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ , as demonstrated in a comprehensive review paper (Beaumelle *et al.* 1993). These values are still insufficient for the practical application according to the economic analysis of a commercial-scale fuel ethanol plant. As reported by O'Brien *et al.* (2000), if the pervaporation performance could be improved modestly to exhibit the flux of  $150 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  and a separation factor of 10.3 for ethanol to water, a coupling system would be cost-competitive. In an attempt to improve membrane performance in terms of selectivity, flux, and mechanical strength, PDMS membranes have been modified with various physical and chemical methods, including filling, grafting (Bennett *et al.* 1997), copolymerization (Wu *et al.* 2001), blending (Miyata *et al.* 1996), and organofunction (Bennett *et al.* 1997).

Filling a polymer membrane with a particulate material to form the so-called mixed-matrix membranes (MMMs) is a physical technique examined in a number of studies. Active carbon,

carbon black, zeolite molecular sieves, carbon molecular sieves (CMSs), fumed-silica, and magnesium oxide (Jiang *et al.* 2007) are alternatively prevalent choices. Adnadjevic *et al.* (1997) determined the pervaporation properties of PDMS membranes filled with several kinds of hydrophobic zeolites. An increase in the zeolite content resulted in an increase in both the membrane permeability and selectivity, but the flux is still low. Additionally, the physicochemical characteristics, predominately the degree of hydrophobicity, as well as sorption capacity, specific pore volume, specific area, and crystallite size, strongly influence the pervaporation properties of the membranes. Ye *et al.* (2005) studied the pervaporation for removing ethanol from an aqueous solution with carbon black-filled PDMS membranes. It indicated that the permeation rate increased with the carbon black content in the membranes, whereas the selectivity of the filled membranes for ethanol recovery was almost consistent with that of the unfilled membranes. However, the carbon black content was less than 5 wt% with respect to PDMS, and the permeation rate of the membrane decreased dramatically with N330-type carbon black when the filler content was more than 3 wt%. In this paper, we present an overview of the ethanol recovery by pervaporation using PDMS-based membranes with adsorbents incorporated. Even though several reviews of pervaporation using polymeric materials have become available in recent years (Shao and Huang 2007, Smitha *et al.* 2004, Rautenabach *et al.* 1992, Chapman *et al.* 2008), no in-depth paper is devoted to systematically summarizing the progress of adsorbent-filled PDMS membranes. Furthermore, it seems that zeolite and nanofumed silica have been the most studied and have governed the research field of MMMs. In the following sections, we primarily review the performance of adsorbent-filled rubbery membranes. In addition, the fundamental of ethanol and water transport mechanisms through membranes is also demonstrated, particularly from the perspective of cluster formation. Finally, potential future research and recommendations on ethanol permselective membranes by pervaporation are also suggested.

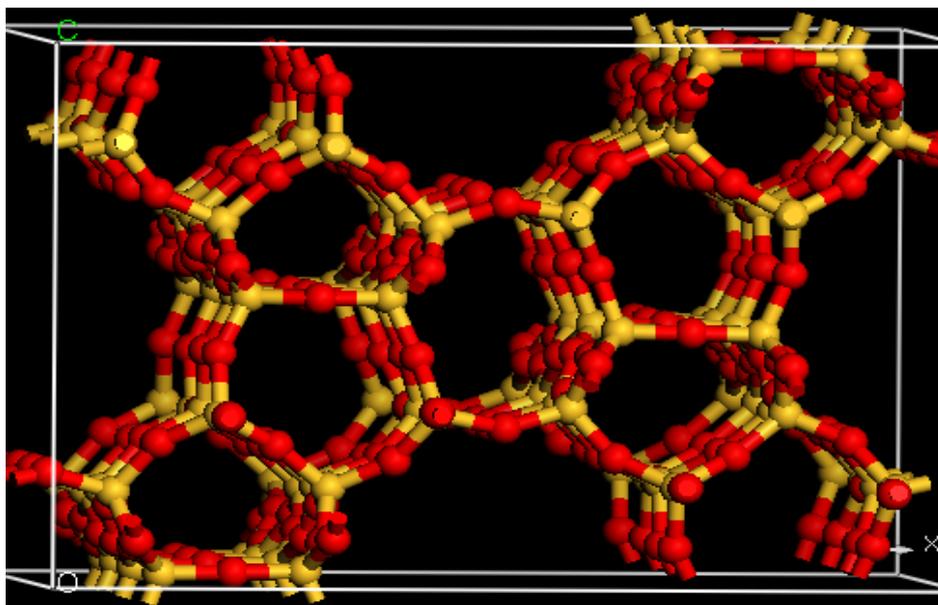


Fig. 1 Atomic ball and stick representation for the framework of MFI structure. The nodes represent tetrahedral framework atoms and the sticks represent oxygen bridges

## 2. Zeolite molecular sieves

Until now, several adsorbents have been studied. But according to the amount of observation, zeolites are the most prevalent and exhibit considerably excellent separation performance. Zeolites are hydrated aluminosilicates with crystalline structures that have uniform molecular-sized pore sizes between 0.3 and 1.0 nm. For the small pore sizes, molecules can adsorb and diffuse via these pores with different diffusion rates depending on their inherent properties such as molecular size and adsorption strength inside the zeolite crystals. Additionally, with decreasing aluminum content, their characters change from hydrophilic to hydrophobic (Nakamoto and Takahashi 1982). Because of their high surface area (up to 1000 m<sup>2</sup>/g), high void volume, and uniform pore-size distribution, zeolites have been widely used in chemical and physical processes such as shape-selective catalysis and adsorbents. More recently, polycrystalline zeolites have been blended into the silicon rubber to synthesize typical MMMs for enhancing pervaporation performance. Te Hennepe *et al.* first reported the preparation of zeolite-filled membranes for ethanol recovery in 1987 (Te Hennepe *et al.* 1987). The result presented in the paper indicated that when the silicalite content increased from 0 to 70 wt%, a significantly improved ethanol-permselective performance with a separation factor of 7 up to as high as about 40 was obtained. The flux also increased from 0.02 to 0.045 L·m<sup>-2</sup>·h<sup>-1</sup>, implying a facilitated transport of ethanol molecules through the silicalite. Since then, significant progress has been made to improve the quality of zeolite-filled membranes and widen their scope of utilization. Today, the MFI structure is most commonly used in zeolite-filler composite membranes because of its pore size and ease of preparation. The model of the MFI structure is shown in the ball-and-stick representation of zeolite framework in Fig. 1. Silicalite-1 and ZSM-5 are the representatives of MFI-type zeolite (Yuan *et al.* 2004). The main difference between ZSM-5 and silicalite-1 is the aluminum content, which is nil for the latter (Bowen *et al.* 2004). The aluminum atoms in the lattice are so scarce that both zeolites behave as hydrophobic and organophilic sorbents (Olson *et al.* 1980, Flanigen *et al.* 1978), and they could also selectively adsorb organic molecules over water.

Table 1 Ethanol-water separation performances of PDMS membranes with different fillers

Fillers	Content (wt%)	Concentration of feed (wt%)	Temperature (°C)	Separation factor	Flux	Reference
Zeolite	60	5	22.5	16.5	51 g·m <sup>-2</sup> ·h <sup>-1</sup>	Te Hennepe <i>et al.</i> 1987
USY	50	5	30	16.1	610 L·m <sup>-2</sup> ·h <sup>-1</sup>	Adnadjević <i>et al.</i> 1997
ZSM-5	50	5	30	14	460 L·m <sup>-2</sup> ·h <sup>-1</sup>	Adnadjević <i>et al.</i> 1997
Carbon black	4.5	13.73	20	10.1	127.3 g·m <sup>-2</sup> ·h <sup>-1</sup>	Ye <i>et al.</i> 2005
Carbon black	10	6	35	8.5	49.8 g·m <sup>-2</sup> ·h <sup>-1</sup>	Vankelecom <i>et al.</i> 1997b
Fumed silica	20	5	40	7	–	Tang <i>et al.</i> 2007
Nano-silica	5	5	60	30.1	114 g·m <sup>-2</sup> ·h <sup>-1</sup>	Sun <i>et al.</i> 2013
Zeolite (CBV3002)*	30	3	41	5.5	151 g·m <sup>-2</sup> ·h <sup>-1</sup>	Dobrak <i>et al.</i> 2010
ALPO-5	50	5	30	5.2	200 L·m <sup>-2</sup> ·h <sup>-1</sup>	Adnadjević <i>et al.</i> 1997
ZSM-5	30	6	35	5	250 g·m <sup>-2</sup> ·h <sup>-1</sup>	Vankelecom <i>et al.</i> 1995
Zeolite Y	30	6	35	4.5	750 g·m <sup>-2</sup> ·h <sup>-1</sup>	Vankelecom <i>et al.</i> 1995

\* A commercially available silicalite

Table 2 Comparison of ethanol-water separation performances of different silicalite-1/PDMS hybrid membranes

Loading (wt%)	Modifier/treating agents	Concentration of feed (wt %)	Temperature (°C)	Separation factor	Flux ( $\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ )	Reference
77	Self-synthesized	70	22	59	71	Jia <i>et al.</i> 1992
65	Unmodified	5	50	43.1	–	Vane <i>et al.</i> 2008
50	Unmodified	4.4	50	12.2	80	Chen <i>et al.</i> 1998
50	0.5 mol/L HCl	4.4	50	18.2	130	Chen <i>et al.</i> 1998
50	Water stream	4.4	50	18.8	70	Chen <i>et al.</i> 1998
50	HCl-water stream	4.4	50	29.3	75	Chen <i>et al.</i> 1998
60	Unmodified	5.3	50	21	105	Yi <i>et al.</i> 2010
60	*VTES	5.3	50	26	100	Yi <i>et al.</i> 2010
67	*VTES	5.3	50	32	95	Yi <i>et al.</i> 2010
30	*MSTFA-nano-sized	6.0	35	15.7	70	Moermans <i>et al.</i> 2000
30	Silylated-nano-sized	6.0	35	13.9	85	Moermans <i>et al.</i> 2000
40	*MSTFA-nano-sized	6.0	35	16.4	100	Moermans <i>et al.</i> 2000
30	*MIBK	6.0	35	10	350	Vankelecom <i>et al.</i> 1995
50	*MIBK	6.0	35	7	–	Vankelecom <i>et al.</i> 1995
15	Unmodified	3	41	4.8	170	Dobrak <i>et al.</i> 2010

\*VTES: vinyltriethoxysilane; MSTFA: *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide; MIBK: Methyl isobutyl ketone

### 3. Mixed-matrix membranes (MMMs)

In recent years, much research on the potential of MMMs has been conducted. An overall review of membrane materials for ethanol recovery was written by Peng *et al.* in 2011 (Peng *et al.* 2011a). Bowen *et al.* prepared some Sandwich – type PDMS composite membranes which include a pure PDMS top coat, a ZSM-5 zeolite/PDMS middle layer and an UF membrane support layer (Bowen *et al.* 2007). They found that when 65 wt% ZSM-5 zeolite/PDMS was prepared as the middle layer, twice of the fluxes and separation factor were obtained when compared with the pure PDMS membranes, which were up to  $521 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  and 18, respectively (Bowen *et al.* 2007). Offeman *et al.* (Offeman and Ludvik 2011) fabricated a thin-film composite (TFC) membrane based on transfer of a preformed and cured active layer onto a microporous support. A selectivity of 0.76 and total permeance of  $199 \times 10^{-8} \text{ kmol}/(\text{m}^2\cdot\text{kPa})$  were obtained, respectively. The composite PDMS membrane supported by CA microfiltration membrane was successfully prepared by adding nano-fumed silica particles with silane coupling reagent in the work of Peng *et al.* (2011b). They also used response surface methodology to optimize the preparation conditions. According to their analysis, when an ethanol aqueous solution with a concentration of 10 wt%, the maximum selectivity of 19 could be obtained at the feed temperature of 40°C, and the corresponding permeation flux was  $200 \text{ g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ . Tables 1 and 2 list the ethanol-water separation performance reported in the literature for inorganic filler–PDMS MMMs. The range of ethanol separation factors observed in the research, 2.3 to 59, overlaps the range reported for both PDMS and silicalite-1 alone. Actually, as a dense pervaporation membrane of PDMS/silicalite-1 MMM,

PV 1070 was commercially available from Sulzer Chemtech (Neunkirchen, Germany); however, it was removed from the market several years ago.

#### 4. Parameters influencing separation performance

Based on the above information, it was found that pervaporation performance was significantly influenced by the membrane compositions and the preparation parameters. The following methods are identified from the literature (Vane *et al.* 2008) as potentially important to membrane performances:

- (1) Particles should be well dispersed and agglomerations should be disrupted. Sonication is the most useful method (Tang *et al.* 2007, Vankelecom *et al.* 1994, Huang and Meagher 2001).
- (2) The surface chemical properties of particles may need to be altered. Acid and/or steam treatment (Long *et al.* 1994, Bowen *et al.* 2004) and/or silylation should be considered.
- (3) The smallest-diameter particles intuitively lead to the ability of making the thinnest possible defect-free membranes. However, the tendency of particles to agglomerate (and with it the tendency to form defects and reduce separation performance) is inversely related to particle size (Mahajan *et al.* 2002, Chung *et al.* 2007).
- (4) Even though pre-crosslinking of the silicone rubber may be favorable, it is not definitive in obtaining the best result. It is likely that the silicon rubber system used greatly relates to the result.
- (5) Moisture should be avoided when preparing membranes because water can alter the surface chemical properties of the particles or interfere with reactions; therefore, particles and/or solvents should be dried prior to use.
- (6) Higher particle loading is not always necessary to achieve the best result. A certain amount of particle loading always occurs, which mainly depends on the thickness of membranes.
- (7) Generally, zeolite particle loading as high as 77 wt% is possible, but some systems may be limited to a maximum of 30 wt% because of particle agglomeration and defect formation (Jia *et al.* 1992, Dobrak *et al.* 2010).

Vane *et al.* (2008) studied several of the parameters listed above to assess their importance on the ethanol-water separation performance of MMMs. The results demonstrated that the three parameters that most influenced membrane performance are: uniform particle dispersion, high zeolite loading, and particle size (particularly as it relates to particle agglomeration). All of them had also been identified as important in the literature. The three least-important parameters were: catalyst level, pre-crosslinking of the silicon rubber, and avoidance of moisture in the raw materials; the last two of which had been identified as important in one or more of the references. In addition, only the alteration of particle surface chemical properties was not evaluated in their work.

The maximum separation performance of MMMs was especially restrained by a variety of interfacial defects and non-idealities, including leaky interface, zeolite aggregation, and defects and barriers in zeolites (Te Hennepe *et al.* 1987, Jia *et al.* 1992, Nobel 2011). In an attempt to overcome the interfacial defects and non-idealities, numerous studies have focused on the modification of surface physiochemical properties of raw zeolites. Despite the unevaluated

importance of alternation of particle surface chemical properties on membrane performance, it definitely plays a crucial role in the separation processes. Chen *et al.* (1998) studied the effect of HCl acid and water steam treatment of silicalite-1 on the pervaporation performance of zeolite-filled PDMS membranes. Zhan *et al.* (2010) reported that modification of silicalite-1 with chlorosilanes was an effective way to improve the integration with the PDMS matrix and the selectivity of MMMs for ethanol. Moreover, the silicalite-1 particles were modified by a silane coupling agent, vinytriethoxysilane (VTES), and incorporated into the PDMS matrix for the preparation of silicalite-1/PDMS hybrid membranes in the work of Yi *et al.* (2010). The chemical crosslinking involving a reaction of surface vinyl groups on the modified silicalite-1 with the polymer enhanced the stability of the membranes and reduced the potential for membrane swelling. The silylation could also increase the polymer matrix from 60 wt% for the unmodified silicalite-1 to 67 wt% for the modified silicalite-1, and consequently increase the selectivity of the hybrid membranes. Similarly, Wang *et al.* (2012) successfully synthesized MCM-41 mesoporous silica spheres via modified Stober method (Grun *et al.* 1997) and modified them using three kinds of silane coupling agents with different alkyl chain lengths. The calcined and modified mesoporous MCM-41 spheres were incorporated into PDMS polymers for the first time to form the filled membranes. It is obvious that modified MCM-41 spheres exhibited outstanding interfacial adhesion with hydrophobic PDMS membrane matrix. Moermans *et al.* (2000) treated the nano-sized silicalite-1 with a silane coupling agent *N*-methyl-*N*-(trimethylsilyl) trifluoroacetamide (MSTFA) to cover the surface with hydrophobic trimethyl groups. The results showed that silylation had a positive effect on the maximum amount of zeolite. Surprisingly, compared with the non-silylated zeolite-filled PDMS membranes, the membrane selectivity of ethanol decreased in the same loading after silylation. Vankelecom *et al.* (1997b) incorporated three types of hydrophobic porous fillers (carbon blacks, in-situ methylated silicas, and silylated silicas) that were changed systematically into PDMS silicon rubber membranes to maximize fluxes and selectivities in the pervaporation of aqueous ethanol. Silicas silylated with trimethylchlorosilane (TMCS) were found to be the best filler when applying feed mixtures that induced low swelling in the membrane.

All of the modification methods mentioned above were moderate to improve the interfacial integration and pervaporation performance by increasing the organic constituents on the zeolite surfaces or eliminating impurities in the zeolite inner pores. Few studies focused on the effect of zeolite surface morphology on interfacial integration and pervaporation performance of MMMs.

In another study of Zhan *et al.* (2012), the incorporation of surface etched MFI zeolite with hydrofluoric (HF) acid into PDMS membranes and the zeolite surface morphology on interfacial integration and pervaporation performance of MMMs were reported for the first time. The result indicated that etched ZSM-5-filled PDMS membranes exhibited high tensile and swelling resistance because of the tight integration of PDMS and zeolite phases, which stemmed largely from the intrusion of PDMS polymer into micro-sized pores out of the zeolite surface created by HF etching. Moreover, as the HF acid concentration increased from 0 to 0.056 g/mL, the separation factors increased drastically from 9.2 to 16.7, but the flux decreased from 148.6  $\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  to 133.8  $\text{g}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ , oppositely. In addition, both ethanol permeation and selectivity increased as the zeolite loading increased from 10% to 30%. Nevertheless, excessive zeolite loading or decreasing thickness of the selective layer led to the poor selectivity to ethanol.

## 5. Pervaporation fundamentals

Because the fundamental pervaporation process is combined inherently with the separation performance, many studies have been conducted to clarify the mechanism of pervaporation. The models used to explain the transport mechanism of ethanol/water mixtures are generally based on the solution-diffusion mechanism (Miyagi *et al.* 2012, Kujawski *et al.* 2007, Heintz and Stephan 1994), the Flory-Huggins theory (Lin *et al.* 2004), the hydrophobic sorption model (Kokugan *et al.* 1998), and the Maxwell-Stefen theory (Nagy 2004). Among them, the theoretical solution-diffusion mechanism is widely accepted to describe the mass transport process through dense membranes because of its good agreement with experiments (Wang *et al.* 2001, Wijmans and Baker 1995). The solution-diffusion model is a semi-empirical or phenomenological model originally proposed by Graham (Lonsdale 1982) based on his extensive research on gas permeation through homogeneous membranes. It mainly states that pervaporation consists of three consecutive steps: (i) the permeant dissolves in the upstream surface of the membrane; (ii) the permeant diffuses across the membrane matrix; and (iii) the permeant evaporates as vapor at the downstream side of the membrane. Several mathematical equations for the rate-controlling transport process have been formulated on the basis of the Fick's first law (Wu *et al.* 2001). However, the existing direction of the theories is still not mature enough to describe the separation system (Lue *et al.* 2012). The diffusion process for the ethanol-water mixture is more complicated because water and ethanol tend to form hydrogen bonds and may aggregate in a polymer matrix. The formation of hydrogen bonds among water-water molecules, ethanol-ethanol molecules, and water-ethanol molecules in a polymer matrix is probable. Favre *et al.* (1994) analyzed the transport of water and a series of alcohol vapors through dense silicon rubber membranes using the vapor permeation technique. It was suggested that some clustering behaviors existed inside the PDMS during the process. Watson and Baron (1996) investigated the water behavior by statistical-mechanical method and observed that the diffusion coefficient of water in PDMS was nearly constant over a wide activity range; hence, the incidence of the statistical clustering of water within the polymer was negligible. Tamai *et al.* (1994) and Fritz and Hofmann (1997) used a molecular simulation technique to investigate the diffusion of water and ethanol through PDMS. The former revealed that the diffusion coefficients of ethanol and water were diminished by more than one order of magnitude because of the aggregation. The calculated diffusion coefficient of the nonaggregated penetrants in PDMS and in pure liquids agreed well with the experimental values. The latter indicated that water and ethanol did not aggregate inside PDMS. Radovanovic *et al.* (1990) studied the pervaporation process of ethanol and water through silicon rubber membranes based on the assumption that water clusters, practically immobilized within the membranes, breaking down to form mobile ethanol-water dimers in the presence of ethanol; ethanol and water molecules could partly be transported as ethanol-water dimers. The result showed that the model was consistent with the experiment data over the whole activity range of water, but at high ethanol activities this model proved unsuccessful to demonstrated ethanol flux behaviors. The molecular dynamic (MD) simulation technique especially provides a promising tool for analyzing transport processes on an atomic scale (Hoffman *et al.* 1998, Gee *et al.* 2004, Muller-Plathe 1991). Nasiri and Aroujalian (2010) investigated pervaporation performance of composite PDMS membranes for the separation of ethanol-water mixtures. The probability of cluster formation into the PDMS matrix was analyzed by the MD simulation technique. Ethanol-water dimerization was evidenced by MD simulation. Cluster formation within water-water and ethanol-ethanol molecules into PDMS failed to be observed even at maximum activity. They proposed a new semi-empirical model for diffusion coefficients based on the ethanol-water dimerization reaction, and the behavior of ethanol and water flux curves versus ethanol feed concentration was very well expressed by this

model. Additionally, the model was used to predict the influence of other operation parameters and prediction results showed excellent agreement with the experimental data. Several articles have been published which described the ethanol-water clusters during the evaporation processes. Tsuchiya *et al.* (2004) introduced the cluster compositions at the liquid surface using liquid ionization mass spectrometry (LPI-MS). They concluded that the number of alcohol molecules in clusters seemed to be one of the most important parameters for estimating the cluster composition in liquids, because these numbers were related to the concentration of solutions. Raina *et al.* (2001) also examined the vapor-phase clusters from ethanol-water mixtures of varying compositions with the aid of a time-of-flight mass spectrometer. Similarly, by analyzing the mass spectra of clusters generated through fragmentation of liquid droplets, the microscopic structures in ethanol-water binary mixtures were investigated by Wakisaka and Matsuura (2006).

## 6. Conclusions

Because flux and separation factors are strongly affected by operation conditions, such as feed concentration, temperature, and permeate pressure, the measured properties of PDMS membranes vary conspicuously between researchers. Many difficulties exist in comparing the pervaporation performances of membranes in the literature. Fortunately, a novel method based on the solution model emerged in a work of Baker *et al.* (2010), which provides a consistent way to compare the performances of dense membranes on a driving-force normalized basis.

Even though probable mechanisms for depicting the pervaporation process have been proposed, they are rarely available for the prediction of the membrane performance. Meanwhile, based on the clustering-formation theory, a number of studies have been conducted that focused on the clustering composition and/or the prediction of diffusion and solubility of small molecules through silicon rubber membranes. MD technology especially provides a prevalent tool for analyzing the transport process on an atomic scale. However, much of the explanation only dealt with gas diffusion or the behavior in the bulk or on the surface of liquid mixtures. While these theories and the techniques adopted will contribute immeasurably to the acquisition of direct experimental information about what occurs in molecular dimensions during pervaporation, more appropriate fillers could be selected regarding the interior mechanism. Based on the previous research, a novel method to introduce graphene to the polymer matrix may be considerably available for its special structure.

Historically, unfavorable swelling, which mainly causes the membrane stability to decline, is an inherent obstacle for the industrialization of pervaporation membrane technology, because it can cause the decline of separation abilities with respect to time (Qiao and Chung 2005). Chang *et al.* (2012) adopted the MD simulation technique to analyze several parameters of the PDMS membranes. Their study showed that the swelling of the PDMS membrane resulted in an expanded membrane structure because of the higher ethanol-membrane interaction, which led to a larger cavity. On the other hand, the utilization of crosslinking agents could improve membrane stability (Bueso *et al.* 2000, Osorio-Galindo *et al.* 2001) to a certain degree. To date, most attempts have been made to modify the polymeric materials, but the separation performance and durability of the polymeric membranes could only be improved marginally (Kariduraganavar *et al.* 2009, Chapman *et al.* 2008). The shortcomings of polymeric membranes have spurred the development of new materials and technologies to accomplish the functional requirements of biofuel separation. In addition, the real material properties can only be defined when the membranes are evaluated in

special systems for a long period of time. Thus, great exploratory efforts still need to be made to meet the demand for commercial-scale manufacturing.

## Acknowledgments

The authors would like to acknowledge the financial support by National Natural Science Foundation of China (21376048).

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