Desalination and Water Treatment
www.deswater.com

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doi: 10.1080/19443994.2012.728053

51 (2013) 2368–2376
February

Taylor & Francis
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Ethanol dehydration by pervaporation using microporous silica membranes

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Received 25 November 2011; Accepted 30 April 2012

ABSTRACT

The experimental results of the effect of the conditions of silica layer preparation, such as dip-coating velocity and calcination temperature, on the flux and selectivity of tubular silica membranes in ethanol removal by pervaporation are reported and discussed. Moreover, the influence of the physico-chemical properties of silica materials on membranes performance as a function of their preparation conditions and operation time is studied. The strong effect of silica dip-coating velocity as well as its calcination temperature on membranes performance was observed. The application of a dip-coating velocity of $1\,\mathrm{cm\,s^{-1}}$ and calcination temperature of 400°C let to obtain highly selective membrane with typical fluxes for ceramic membranes. Strong interactions between ethanol and silica resulted in the reduction of total flux and selectivity as function of membrane operation time. The decline in separation performance was attributed to reversible adsorption of ethanol by hydrogen bonding with hydroxyl groups on the silica surface. Pervaporation performance in ethanol dehydration (6 wt.% of water) using the synthesized silica membranes was better than that of commercially available polymeric as well as ceramic tubular membranes. The obtained values of total flux ($0.417\,\mathrm{kg\,m^{-2}\,h^{-1}}$) and selectivity (207) are one of the highest reported in the literature for ethanol dehydration.

Keywords: Microporous silica membranes; Membranes preparation; Ethanol dehydration; Pervaporation

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1. Introduction

Biofuels have attracted increasing interest over the last few decades. Topics such as energy security, economic development, climate change mitigation, and greenhouse gas emissions have potentiated their application. Biofuel ethanol (99.5 wt.%) has been recognized as a potential, eco-friendly, and economic substitute for petroleum-based fossil fuels [1]. Its production engages few important steps between

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International Scientific Conference on Pervaporation, Vapor Permeation and Membrane Distillation, 8–11 September 2011, Toruń, Poland

them: fermentation, ethanol purification, and dehydration. Traditionally, purification and dehydration of ethanol are performed using a multi-column distillation and adsorption systems, respectively. However, the conventional methods for the separation of both azeotropic and close-boiling point mixtures are complex, expensive, and consume a large amount of energy. It has been estimated that ethanol purification and dehydration consume more than half of the total energy required in the alcohol production by fermentation [2].

Membrane-based separation offers a simpler and more energy-efficient method, considering that the separation mechanism is independent of the vapor–liquid equilibrium characteristics of the mixture to be separated. Moreover, it is characterized with compact and modular design as well as the absence of chemical agents required in many other separation processes [3]. According to the literature [4], inorganic membranes offer better thermal, chemical, and mechanical stability in comparison to the polymeric ones. Moreover, they show many operational advantages such as: long lifetime, high fluxes, and wide range of operation conditions, despite their high initial costs [5]. Two kinds of inorganic membranes which are used for the separation of small substances are especially important: hydrothermally synthesized zeolite [6] and sol–gel-derived silica membranes [5]. In general, zeolite membranes are characterized with very narrow pore size distribution and, therefore, are well suited to molecular-sieving separation of some types of molecular mixtures. On the other hand, silica or silica-based membranes present rather wide pore size distribution, consisting mainly of micropores formed as silica network pores and medium-sized pores formed as either interparticle pores and/or grain boundaries. However, both of them have been reported as highly selective and permeable [7]. An advantage of silica-based membranes is that they are relatively low priced. Therefore, pervaporation through microporous silica membranes appears to be a promising and economic alternative for ethanol purification.

Microporous silica membranes have been extensively used in solvents dehydration by pervaporation [8–13]. In the specific case of ethanol purification, several studies have been performed using tubular [8,10] and flat plate [11] silica membranes. As stated by Peters et al. [9], the flat plate geometry membranes are usually characterized with a small surface area (typically $\sim 10^{-2}\,\mathrm{m}^2$) due to limitations imposed on the dimensions by the dip-coating technique, even if they are advantageous from an academic point of view. On the other hand, the surface area of tubular silica membranes is larger and their geometry is also more compatible with the technology developed in organic membrane science. Commercially available membranes for pervaporation have a tubular geometry [9]. Therefore, in this work, silica layers are deposited by dip-coating on the top of tubular ceramic supports which let to relatively low costs and quick membrane preparation.

Several papers [12,13] have already discussed the effect of pervaporation parameters, such as mixture composition, temperature, and permeate pressure, on the performance of silica membranes. However, some details especially related to the specific conditions of membranes deposition, their posterior thermal treatment as well as their performance in pervaporation remain to be identified.

The present study is focused on the effect of the conditions of silica layer preparation, such as dip-coating velocity and calcination temperature, on the flux and selectivity of silica membranes in ethanol dehydration by pervaporation. Moreover, the influence of the physico-chemical properties of silica materials on membranes performance as a function of their preparation conditions and operation time is studied. The prepared silica powders and membranes were characterized using different techniques, such as TGA, FTIR, SEM–EDS and N_2 physisorption, and evaluated in the dehydration of ethanol (5 wt.% of water) by pervaporation, at 70 °C, close to the azeotropic point characterized with ethanol composition of 95.7 wt.% at 585 mm Hg and 71.65 °C, as calculated using Aspen Plus® software. In order to compare the performance of the membranes prepared in this study with those reported in the open literature, additional pervaporation experiments were performed (6 wt.% of water; 70 °C).

2. Experimental

2.1. Membrane preparation

InoCep® ceramic hollow fiber membranes (Hyflux CEPAration-Netherlands) made of α-Al_2O_3 with length of 30 cm, an inner and outer diameter of 2.0 and 3.0 mm, respectively, and pore size of 200 nm were used as a support. Three intermediate layers of γ-alumina and, on top, three layers of silica were deposited by dip-coating at room temperature in a cupboard to minimize dust contamination. Corresponding γ-alumina and silica layers were deposited using boehmite sol and silica gel solution, respectively.

Boehmite (γ-AlOOH) sol was synthesized according to the procedure presented by Peters et al. [9]. Dip-coating velocity of $3.3\,\mathrm{cm\,s^{-1}}$ was used to obtain a layer thickness of ca. 4 μm [14]. Next, each alumina layer was dried at 40℃ for 2 h and calcined at 600℃ for 3 h, with a ramp rate of 1℃ min^{-1}.

Hydrophilic silica gel was prepared by acid catalyzed (HNO_3) sol–gel method, using the following TEOS (1):ethanol (3.8):water (6.4):nitric acid (0.085) molar ratio [15,16]. The synthesis was based on the hydrolysis and subsequent polycondensation of tetraethyl orthosilicate (TEOS) (Merck, purity > 99%) dissolved in ethanol (Merck, purity > 99.9%). The final density and viscosity of the obtained silica gel were 0.79 g cm^{-3} and 1.29 cP, respectively. As synthesized gel was divided in two parts, one part was used for silica membranes deposition and another one was kept as prepared (powder silica xerogel). Silica layers deposition was performed on top of previously deposited γ-alumina layers using three different dip-coating velocities (0.5, 1.0, and 1.5 cm s^{-1}). Each deposited silica layer was dried at 40℃ for 30 min and calcined in air, at different temperatures (400–500℃), for 4 h, with a ramp rate of 0.5 ℃ min^{-1}. Similar conditions of drying and calcination were used for silica xerogels powders.

2.2. Characterization techniques

Dynamic viscosity of silica gel solution was determined using a Höppler viscometer (Sheen Instrument, UK) and density was measured using a 5 ml pycnometer (Duran, Germany), calibrated with distilled water at 20℃.

TGA–DTA–MS analyses were performed on powder, dried silica xerogel using a Setsys 16/18 (Setaram, France) TGA–DTA instrument, coupled with a quadrupole mass spectrometer (Balzers Thermostar, Liechtenstein). The alumina (Al_2O_3) crucible containing approximately 20 mg of sample was heated from room temperature up to 800℃, in air (40 cm^3 min^{-1}), with a ramp rate of 1℃ min^{-1}. Corresponding m/z values 17 (OH^+, H_2O), 18 (H_2O^+, H_2O), 44 (CO_2^+, CO_2), and 46 (NO_2^+, NO_2) were monitored by mass spectrometry.

Morphological studies of silica and alumina membranes were performed using a S-4700 scanning electron microscopy (SEM) (Hitachi, Japan) coupled with energy dispersive spectrometer (EDS) (Thermo Noran, USA) at an acceleration voltage of 25 kV. For those studies, membranes were cut into a cylindrical shape of 1.5 cm of length. The SEM and EDS studies were carried out in the cylinder's cross and lateral sections, respectively. The examined samples were placed on carbon plasters in a holder and before analyzing were coated with a carbon monolayer using Cressington 208 HR system (Scientific Instruments Ltd., UK), in order to reduce the charge build-up on the samples.

The FTIR characterization of powder silica xerogels, calcined at different temperatures, was performed in a Nicolet 6700 FTIR spectrometer (Thermo Scientific, USA) with MCT detector (photoconductive detector HgCdTe) using a standard sample holder. Transmittance measurements were performed using KBr technique. Pellets were prepared with 5 wt.% of silica and 95 wt.% of potassium bromide (KBr) pressed at 1,800 psi for 5 min. FTIR spectra were recorded in the mid-infrared range of 4,000–400 cm^{-1} at room temperature.

FTIR *in situ* studies of the adsorption of gaseous mixture ethanol–water–argon with the molar percentages 27.6, 3.7, and 68.7%, respectively, were carried out on powder silica xerogels using a high temperature and high pressure cell unit with automatic temperature controller (Specac, UK). Ethanol concentration in the gas phase was obtained after pressurization of ethanol (95 wt.%) with argon up to 10 bar. Approximately, 20 mg of silica powder were pressed at 122 bar for 10 min to obtain a pellet which was placed in the cell unit. After 30 min of adsorption process at 30℃, the temperature of the cell, with the sample inside, was increased and a desorption FTIR spectrum of the sample in argon atmosphere using the Nicolet 6700 FTIR spectrometer (Thermo Scientific, USA) was recorded. Additionally, the spectrum of ethanol–water–argon gas mixture was recorded to identify the bands related with ethanol and water adsorbed on silica surface.

The specific surface area, pore volume, pore size, and their distribution were measured for powder silica xerogels by N_2-physisorption at liquid nitrogen temperature using a Gemini 2360 (Micromeritics, Germany) surface area analyzer. Prior to the measurement, samples were degassed for 8 h at 200℃. The specific surface area was calculated according to the BET theory [17], while the pore size, their distribution, and the pore volume were calculated using the Horvath and Kawazoe (HK) method [18] for microporous materials.

Silica membranes were tested by pervaporation at 70℃ of an ethanol–water mixture (5 and 6 wt.% of water). A stainless steel tubular module has been used to place the silica membrane. The effective length of the membrane was 27 cm (3 mm OD) with an effective membrane area of 0.00254 m^2. On the membrane feed side, a recycle stream was applied in connection with the storage vessel. On the permeate side vacuum was kept below 3 mbar with a vacuum pump. A liquid nitrogen cold trap was used to collect the permeate for further analysis. The retentate compositions were analyzed using an automated Karl–Fischer titration apparatus SM 702 titrino (Metrohm, Switzerland), while the permeate compositions were measured by Elite LaChrom HPLC (VWR Hitachi, USA). Membrane performance was evaluated based on the mass flux across the membrane and selectivity. Permeation flux was calculated from the mass of permeate collected in a cold trap immersed in liquid nitrogen by unit of time and effective membrane area. The overall membrane selectivity (α) is defined as:

$$\alpha = \frac{y/(1-y)}{x/(1-x)} \tag{1}$$

where y and x are water weight fractions in the permeate and retentate, respectively.

3. Results and discussion

The results of standard (in air) TGA–DTA–MS measurements of dried powder silica xerogel are presented in Fig. 1 and summarized in Table 1.

The TGA thermograms exhibit three main regions of weight loss. Through the first weight loss region of ca. 28%, the temperature range of 15–150°C (section A, Fig. 1), the desorption of physically adsorbed and/or trapped in the xerogel network water and ethanol (with a maximum at ca. 50 and 80°C, respectively) as well as the decomposition of the residual nitric acid (with a maximum at ca. 90°C) used as a catalyst during the xerogel synthesis occurs, as confirmed by MS studies (Table 1). In this temperature range, an endothermic peak in DTA curve, with the maximum at ca. 65°C was also present, confirming the observed effects. The second weight loss region of ca. 4%, in the temperature range of 150–400°C (section B, Fig. 1), could be assigned to the removal of residual organic compounds and further polymerization of the silica network. The presence of H_2O^+ ($m/z = 18$) and CO_2^+ ($m/z = 44$) species in the MS spectrum (with a maximum at ca. 230 and 275°C, respectively) confirms this statement. At 400°C, the total weight loss of hydrophilic silica xerogels is about 32%. The further weight loss of ca. 2%, at temperature above 400°C (section C, Fig. 1), could be related to the removal of OH-groups from the silica surface. Considering that the hydrophilic character of silica surface can be advantageous for the separation of ethanol–water mixture rich in ethanol (separation can occur according to the adsorption–diffusion model, instead of pore size exclusion effect), the temperature of 400°C was proposed for the calcination of silica membranes.

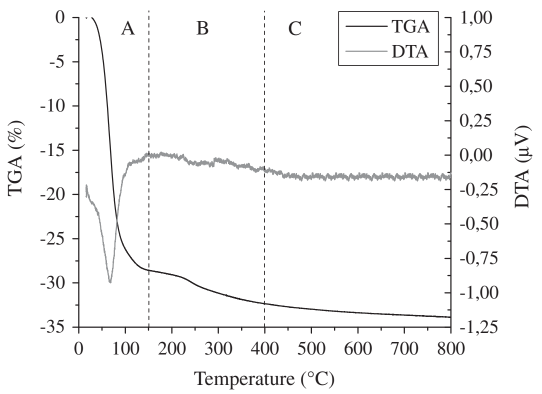

Fig. 1. TGA–DTA studies of silica xerogel in air atmosphere.

The powder silica xerogel calcined at 400°C was characterized with a narrow pore size distribution, with a maximum at 17 Å, which correspond to microporous material. Pore volume, porosity, and specific surface area of silica xerogel were 0.2686 $cm^3 g^{-1}$, 37%, and 518 $m^2 g^{-1}$, respectively.

Fig. 2 presents a typical cross-section of intermediate γ-alumina layers deposited on top of the tubular ceramic membrane support (Fig. 2a) as well as silica layer deposited with dip-coating velocity of 1 $cm\,s^{-1}$ on top of the intermediate γ-alumina layers (Fig. 2b and c).

The presence of γ-alumina layers decreases the support roughness (Fig. 2a), providing to the formation of a smooth surface, ready to deposit silica on the top of it. Moreover, the deposited γ-alumina layers form a homogeneous layer with the thickness of ca. 4 µm, as estimated using the MeasureIT software. Three different characteristic morphologies in the membrane's cross-section can be observed (Fig. 2b): the first one, rough, attributed to ceramic support providing mechanical stability to silica membrane; the second one, smooth, assigned to γ-alumina layer deposited on the top of ceramic support; and the last one, observed as a bright line in the outer size of the membrane, associated with silica layers deposited over the γ-alumina one. The presence of silica on the top of the intermediate γ-alumina layer was confirmed by X-ray energy dispersive spectroscopy (EDS) studies. However, the quantification of its layer thickness was impossible due to the low intensity of silicon on EDS spectra and the difficulty to establish clearly the limit between γ-alumina and silica layer, as it could be seen in Fig. 2c. This result is not surprising considering the visible difference between the appreciable thickness of γ-Al_2O_3 layer (4 µm) and that of silica (Fig. 2b).

The effect of dip-coating velocity and calcination temperature on selectivity and water and ethanol fluxes is presented in Fig. 3. Silica membranes deposited with a dip-coating velocities of 0.5 $cm\,s^{-1}$ and

Table 1
Summary of MS results (in air) for silica xerogel

Mass number (m/z)	Temperature (max. intensity) (°C)	Temperature range (°C)	Key fragments	Probable parent molecule
17	50	15–150	OH^+	H_2O
18	50	15–150	H_2O^+	H_2O
18	230	170–320	H_2O^+	H_2O
44	77	50–150	$C_2H_4OH^+$	C_2H_5OH
44	275	200–350	CO_2^+	CO_2
46	90	40–130	NO_2^+	NO_2

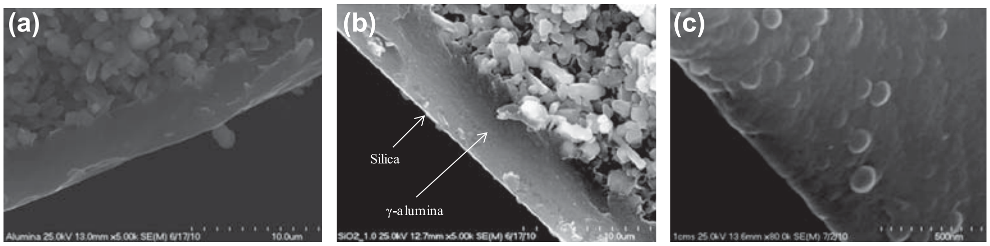

Fig. 2. SEM micrographs of (a) cross-section of the intermediate γ-alumina layers deposited on the top of tubular ceramic membrane support (magnifications 5,000×), (b) and (c) cross-section of hydrophilic silica membrane deposited with dip-coating velocity of 1 cm s^{-1} on the intermediate γ-alumina layers (magnifications 5,000× and 80,000×, respectively).

1.5 cm s^{-1} present significantly lower selectivity than that deposited with an intermediate one of 1.0 cm s^{-1} (Fig. 3a). Moreover, an increase in silica dip-coating velocity leads to a decrease in total flux. It could be expected that silica dip-coating velocity is directly related to its layer thickness and influences the membrane performance in pervaporation process. Low deposition velocities (0.5 cm s^{-1}) probably lead to the formation of thin silica films which have low resistance to thermal treatment. Consequently, during drying and calcination processes microfractures of the silica layer took place and low selective membrane was obtained. On the other hand, high deposition velocities can lead to the formation of thick silica layers which are more resistant to ethanol and water diffusion through the membrane. Therefore, silica membrane deposited with dip-coating velocity of 1.5 cm s^{-1} presented a significant reduction in total flux as compared to the membranes prepared at lower dip-coating velocities. The membrane prepared with a dip-coating velocity of 1 cm s^{-1} has a similar flux to those reported in the literature [8] and high selectivity. This membrane will be used for the subsequent studies.

The strong effect of membrane calcination temperature on its performance in the pervaporation process was also observed (Fig. 3b). Under increasing calcination temperature, a continuous decrease in total as well as in water flux was observed; while the ethanol flux increased. In order to explain it, the FTIR studies of powder silica xerogels calcined at different temperatures are presented in Fig. 4. The hydrophilic nature of silica is attributed to the presence of hydroxyl groups (–OH) on silica surface, evidenced as broad bands at 3,748 cm^{-1} and 3,400–3,500 cm^{-1} at FTIR silica spectrum (Fig. 4). This characteristic bands can be related to the presence of groups (Si–OH) and O–H stretching bands, caused by hydrogen-bonded water molecules (H–O–H$\cdots$H) and surface silanol groups hydrogen-bonded to the molecular water (SiO–H$\cdots$$H_2O$) [19]. Moreover, the hydrophilic nature of the silica xerogel can be related to the presence of the band at 1,640 cm^{-1} (Fig. 4), corresponding to the water vibration adsorbed on silica surface as well as at 960 cm^{-1}, assigned to Si–O in plane stretching vibrations of the silanol (Si–OH) group. The other characteristic bands observed in the range of 1,200–1,000 cm^{-1} as well as at 800 cm^{-1} are related to the antisymmetric and symmetric vibration between Si–O–Si with the minimum at 1,076 and 801 cm^{-1}, respectively. The vibration mode appearing at 1,231 cm^{-1} can be assigned to the symmetric deformation of C–H in CH_2 groups, corresponding to residual nonhydrolyzed alkoxy groups (–OC_2H_5) on the silica

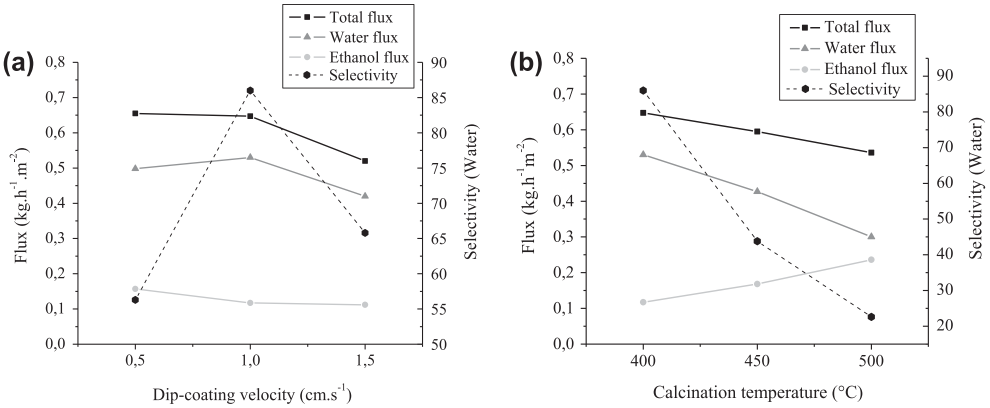

Fig. 3. Silica membranes performance in ethanol dehydration by pervaporation (5wt.% of water, 70°C): (a) effect of silica dip-coating velocity and (b) effect of membrane calcination temperature.

xerogel surface. Under increasing calcination temperature, the continuous loss of silanol groups as well as the reduction in bands intensities at 960 and 3,470 cm^{-1}, related to the –OH interactions, is observed (Fig. 4). It confirms the constant silica surface dehydroxylation and its transformation to a partially hydrophobic material. Consequently, the decrease in the silica's adsorption capacity to water and the increase in its adsorption capacity to organic molecules take place [14]. Moreover, it could be expected that the increase in calcination temperature results in a formation of a denser material characterized with a smaller pore size (14 Å). It explains the lower water selectivity of the membranes calcined at higher temperatures (Fig. 3b). Therefore, silica membrane prepared with a dip-coating velocity of 1 cm s^{-1} and calcined at 400°C presented better pervaporation performance in ethanol dehydration, compared to the others prepared in this study.

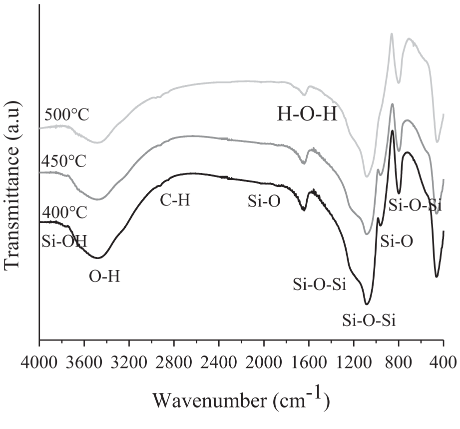

Fig. 4. FTIR spectra of silica xerogels calcined at different temperatures.

Subsequently, three silica membranes were prepared using dip-coating velocity of 1.0 cm s^{-1} and calcined at 400°C. They were characterized with similar properties in the pervaporation of water–ethanol mixture (6 wt.% of water) at 70°C. Fig. 5a shows typical data of the flux and selectivity of one of the studied membranes as a function of time. Representative values for the initial total flux and selectivity were in the range of 0.9–1.5 kg m^{-2} h^{-1} and 20–80, respectively. The steady state of membrane was reached after 12 h of pervaporation, similar to that reported by Ma et al. [8]. The obtained total final flux was 0.417 kg m^{-2} h^{-1} and selectivity was 207. We believe that higher selectivity (207) reported in Fig 5a for the studied membrane, comparing to the value presented in Fig. 3 (85), can be related to both some design improvements that in meantime were made in a cupboard where silica layers were deposited and difference in water content in both series of pervaporation experiments (6 and 5 wt.%, respectively).

Next, the studied membrane was kept in the ethanol–water mixture (6 wt.% water) during 15 days, at room temperature. In this period of time, in order to check membrane's stability, three repeating pervaporation experiments were performed at 70°C, with the total operation time of 2,144 min. Fig. 5b presents typical data of the obtained flux and selectivity as function of a membrane operation time. Notably, the reduction of total flux (15%) and selectivity (20%) as function of membrane operation time is observed. This is attributed to adsorption of ethanol by hydrogen bonding with hydroxyl groups on the silica surface, as confirmed by FTIR *in situ* studies of ethanol–water–argon adsorption on powder silica xerogel (Fig. 6a).

One can see that during the first 5 min of the adsorption experiment, the presence of a new band at

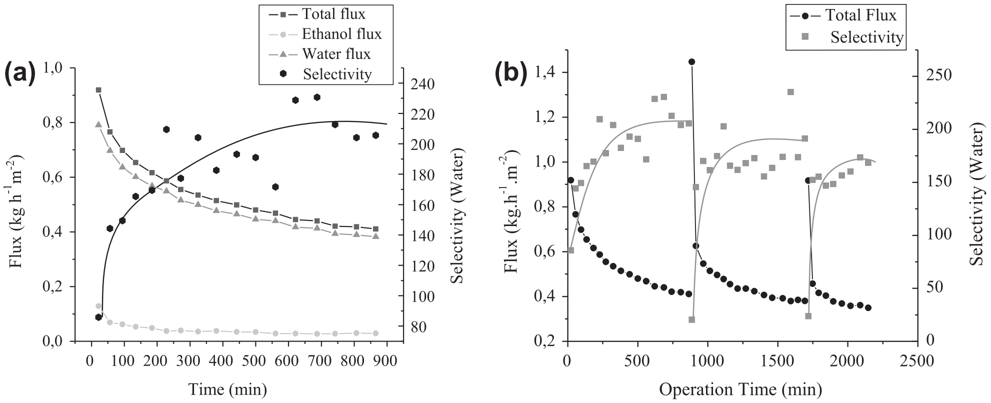

Fig. 5. Silica membrane performance in ethanol dehydration as function of time (6 wt.% of water, 70˚C) during: (a) one cycle and (b) three cycles of pervaporation (lines make obvious the data tendency).

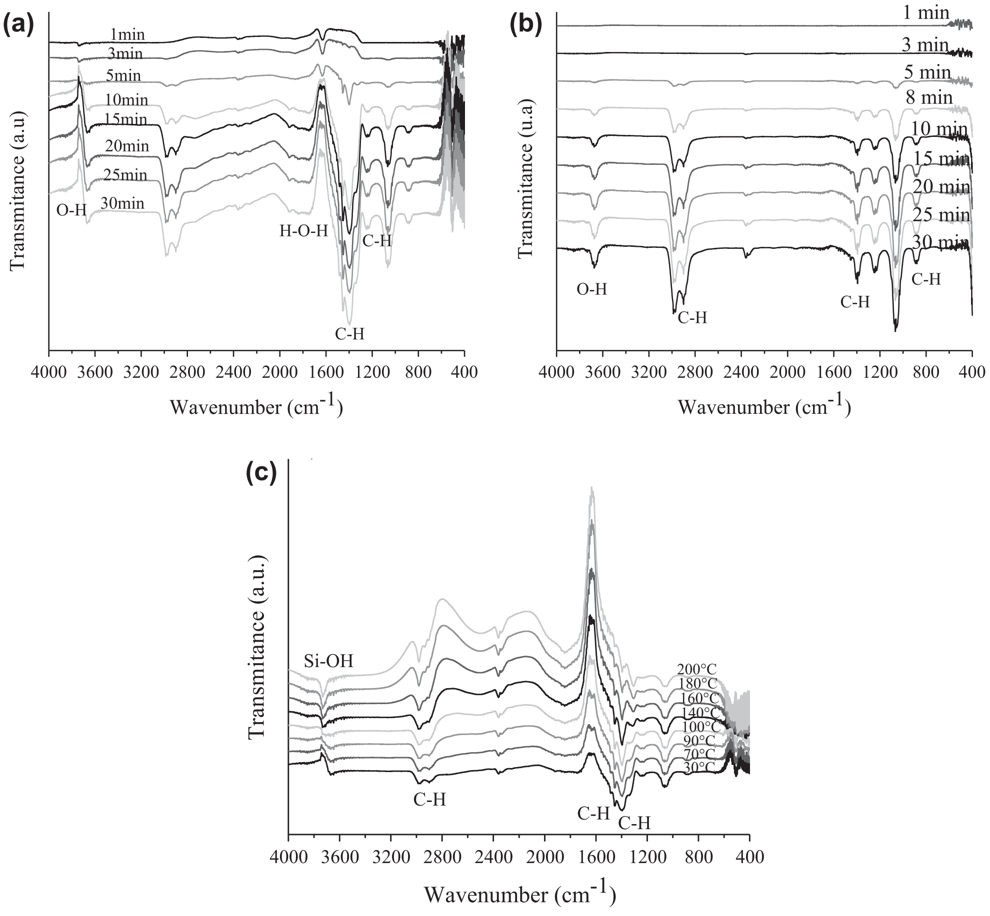

Fig. 6. FTIR spectra of ethanol–water–argon gaseous mixture during: (a) adsorption on silica surface (30˚C), (b) contact with empty measurement and (c) desorption process (30–200˚C).

1,640 cm^{-1}, which is related to the adsorption of water on the silica surface, is observed. Moreover, a band at 3,740 cm^{-1}, characteristic for O–H-isolated silanol group's interactions through hydrogen bond [19] confirms water adsorption on silica surface. After first 5 min, the presence of characteristic bands at 1,454 cm^{-1} and 1,400 cm^{-1}, related to the interactions of symmetric and antisymmetric deformation of bonds

Table 2
Literature data over pervaporation performance of silica membranes in ethanol dehydration

Water concentration (%)	Feed permeate pressure (mbar)	Feed temperature (℃)	Total flux ($\mathrm{kg\,m^{-2}\,h^{-1}}$)	Selectivity	Reference
6	–	70	0.462	97	[8]
6	–	70	0.761	358	[8]
6	–	70	0.31	45	[8]
6	–	70	0.728	20	[8]
6.3	10	60	1.28	25	[10]
6	3–5	70	0.432	12	Hyflux CEPAration
4.5	5	71	1.22	208	[22]
6	3–5	70	0.417	207	This study

in CH_3 groups ($\delta'_{as}(CH_3)/\delta'_s(CH_3)$) [20], and the interactions between C–H in CH_2 groups, respectively, confirm ethanol adsorption. One can see that the most intense band, related to the ethanol adsorption, appears at 1,400 $\mathrm{cm^{-1}}$ which can be associated with δ'_{as}(C–H) interactions. The other bands observed at 1,452 and 1,484 $\mathrm{cm^{-1}}$ can be assigned to the following ethanol–silica interactions: $\delta'_{as}(CH_3)/\delta''_{as}(CH_3)$ and δ' (CH_2), respectively. Moreover, after 30 min of adsorption experiment the absence of characteristic bands at 3,740 and 1,640 $\mathrm{cm^{-1}}$, related to the interactions between H–O and water adsorbed on silica surface, is registered. It suggests that ethanol adsorption takes place on the sites at which earlier water was adsorbed, especially silanols groups, where it can be adsorbed by hydrogen bonds. Consequently, ethanol adsorption renders silica surface more hydrophobic, leading to the decrease in the water flux and selectivity, and preventing permeation, especially in the long period of time. However, it should be noticed that the adsorption of ethanol is a reversible process. The existence of a new band at 1,300 $\mathrm{cm^{-1}}$ and the stronger intensity of a band at 2,898 $\mathrm{cm^{-1}}$, associated with the presence of ethanol in gas phase (Fig. 6b), observed during the desorption process (Fig. 6c), confirm this statement. Moreover, similar values of the initial flux and selectivity of each pervaporation experiment verifies those observations. Concluding, one can see that ethanol adsorption has significant influence both on the membrane performance (its flux and stability) as well as on the time which is necessary to reach the steady stable. This indicates the limited stability of the silica membrane for the separation of ethanol–water mixtures rich in ethanol (6 wt.% of water).

The possible water–ethanol separation mechanism using silica membranes can be based on the hydrophilic nature of the membrane, in accordance with the adsorption–diffusion model [21], instead of pore size exclusion effect [12]. Silica xerogel powders were characterized with pore size of 17 Å, which is higher than the kinetic diameter of ethanol (4.4 Å) and water (2.8 Å) molecules. Therefore, it could be expected that both substances are able to diffuse through the membrane. Silica membrane calcined at 400℃ presented selectivity toward water in the separation process. Considering silica hydrophilic nature, which was confirmed by FTIR studies (Fig. 4), it could be expected that the selective pass of water through the membrane takes place.

Table 2 presents an overview of pervaporation data of various silica membranes in ethanol dehydration recently presented in the open literature, including the results of our study.

One can see that the performance of the tubular silica membrane prepared in this study is comparable to those reported in the literature. The value of its total flux (0.417 $\mathrm{kg\,m^{-2}\,h^{-1}}$) is similar to that reported for most of the studied membranes. Moreover, its selectivity (207) is much higher than that of the commercially available one (Hyflux CEPAration, Netherlands) and is one of the highest reported in the literature for ethanol dehydration using tubular silica membranes. It should be also noted that the studied silica membrane presents much higher fluxes than the polymeric pervaporation membrane (GFT PVA 1000), as reported by van Veen et al. [22].

4. Conclusions

The hydrophilic nature of silica xerogels allows their application as membrane for alcohol dehydration, obtaining high selectivity toward water removal. The strong effect of silica dip-coating velocity on membrane performance was observed. Either thin silica films, characterized with low resistance to thermal treatment, or thick silica layer which are resistant to ethanol and water diffusion through the membrane can be prepared at low or high deposition velocities. The strong effect of membrane calcination temperature on its performance was also observed. A dip-coating velocity of $1\,\mathrm{cm\,s^{-1}}$ produces a membrane with high selectivity and typical flux for silica membranes. Densification of the silica material and decrease in both number of hydroxyl groups and pore size resulted in continuous decrease in total and water fluxes, while ethanol flux increased for the synthesized membranes. Better performance of silica membrane was observed after calcination at 400℃. Strong interactions between ethanol and silica resulted in the reduction of total flux and selectivity as function of membrane operation time. The decline in separation performance was attributed to reversible adsorption of ethanol by hydrogen bonding with hydroxyl groups on the silica surface. Pervaporation performance in the dehydration of ethanol (6 wt.% of water) using the synthesized tubular ceramic silica membranes (dip-coating velocity of $1.0\,\mathrm{cm\,s^{-1}}$ and calcination temperature 400℃) was better than that of commercially available polymeric as well as ceramic tubular membranes. The obtained values of total flux ($0.417\,\mathrm{kg\,m^{-2}\,h^{-1}}$) and selectivity (207) were one of the highest reported in the literature for ethanol dehydration.

Acknowledgments

This work has been supported by Jovenes Investigadores e Innovadores "Virginia Gutierrez de Pineda" 2009 Program financed by COLCIENCIAS and Universidad Nacional de Colombia, Sede Manizales (inter-administrative agreement No. 704 of 2009). The authors are grateful to M.Sc. Eng. P. Malinowski and Ph.D. W. Raróg-Pilecka for help in performing SEM-EDS and BET measurements, respectively.

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