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Preparation of Nanopore Hydroxysodalite Zeolite Membranes by Dry Gel Method

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ABSTRACT

Hydroxysodalite (HS) Zeolite membrane was prepared onto seeded mullite supports using a new crystallization method called Dry Gel Conversion Technique. Molar composition of the starting gel of HS zeolite membrane was SiO_2/Al_2O_3=1.0, Na_2O/Al_2O_3=65, and H_2O/Al_2O_3=1000. X-ray diffraction (XRD) patterns of the membranes exhibited peaks corresponding to the support and the zeolite. The crystal species were characterized by XRD and morphology of the supports subjected to crystallization was characterized by Scanning electron microscopy (SEM). Separation performance of HS zeolite membranes was studied for water-Ethanol mixtures using pervaporation (PV). The membranes showed good selectivity towards water in the water-ethanol mixtures. Water permeates faster because of its preferential adsorption into the nano-pores of the hydrophilic zeolite membrane. In PV of water-ethanol mixtures, the membrane exhibits a hydrophilic behavior, with a high selectivity towards water and a good flux. The best flux and separation factor of the membranes were 2.05 $kg/m^2.h$ and 10000, respectively. In addition, these membranes used for hydrogen separation from CH_4 and it showed high selectivity and permeability ratio to zeolite membrane preparated by conventional method.

Keywords: nanopore, hydroxysodalite, pervaporation, dry gel, zeolite, membrane

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1. Introduction

Zeolites are microporous crystalline materials with a uniform pore size distribution on a molecular scale and with high thermal and chemical stability. The most common method for preparing zeolites is the hydrothermal crystallization at relatively low temperatures and pressures (Kita et al., 2001; Buekenhoudt et al., 2006). New crystallization methods for zeolite synthesis are interesting, as they may enable us to prepare zeolites with new structures, compositions and convenient forms such as membranes and films. In recent years, many efforts have been devoted to the development of methods for the reproducible preparation of high-quality zeolite membranes.

Zeolite membranes are commonly prepared by in situ hydrothermal synthesis onto porous supports. In this case, the support contacts the zeolite precursor gel in an autoclave at a specific temperature and for a certain time; both homogeneous and heterogeneous nucleation occur, and under suitable conditions, the crystals grow to form a relatively continuous zeolite layer. Despite the success of this method to prepare zeolite membranes, there are two main disadvantages: first, some crystals are nucleated and grown in the bulk of the synthesis gel; the incorporation of these crystals into the growing zeolite layer is difficult, and therefore additional defects appear in the final membrane. Second, a considerable excess of water and other reactive (such as silicon and aluminum sources and structure-directing ends) is employed, leading to a more expensive synthesis. The so-called secondary (seeded) growth method uses seed crystals synthesized in absence of the support, and carries out crystal growth under conditions that hinder further nucleation. This obviously reduces the influence of the homogeneous nucleation in the final characteristics of the zeolite membrane. An alternative approach to avoid the homogeneous nucleation and growth of crystals that could impair the quality of the zeolite membrane is to deposit a layer of dry aluminosilicate gel on the support and then transform this gel to the zeolite under the presence of vapors. This has the additional advantage of minimizing the waste reactants (Rao et al., 1998; Hu et al., 2008; Goergen et al., 2009).

The dry gel conversion (DGC) method, where synthesis gel is dried in advance and subjected to crystallization to yield a zeolitic phase in a water vapor environment, is a synthetic method for zeolite materials. This method involves crystallization of dry aluminosilicate gel in the presence of steam. The amount of gel and water required in this method is very small as compared to that used in the hydrothermal method. In addition, dry zeolite synthesis processes have a high economical advantage over conventional procedures. Tubular membranes are preferable to flat ones because of their simpler implementation at an industrial scale. However, to our knowledge none of the research works published until now deals with the preparation of tubular zeolite membranes using a dry gel conversion method (Cheng et al., 2009; Sakthivel et al., 2009).

Zeolite HS membrane is excellent materials for solvent dehydration by PV. The pore size of HS zeolite is 0.3 nm, i.e., smaller than that of the MFI zeolite (0.55 nm). The small pore size of HS zeolite makes the separation of small molecules by difference in size possible. Thus small molecules, such as H_2O (0.27 nm), are expected to be separated from ethanol by molecular sieving or configuration diffusion using HS zeolite membranes (Cunill et al., 2005; Aguado et al., 2009; Amnuaypanich et al., 2009). In this study, nanopore HS zeolite membranes were fabricated by dry gel method and then used to separate water/ethanol mixtures. Zeolite HS layers were coated on external surface of porous tubular mullite supports using dry gel method. These membranes were successfully used for dehydration of water/ethanol mixtures and gas permeation of hydrogen.

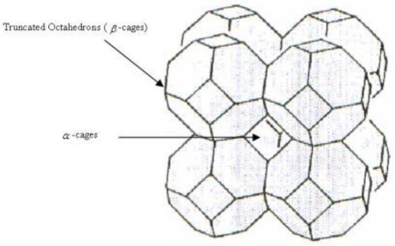

Fig. 1. Repeating unit of zeolite HS

The hydrophilic membranes used in this research were composite zeolite HS membranes. The membranes were made of an active HS layer, deposited on a ceramic porous mullite support. The active HS layer is responsible for high separation factors achieved in PV of ethanol mixtures. The structure of zeolite HS is shown in Fig. 1. As shown in Fig. 1, the aluminosilicate framework of zeolite HS is generated by placing truncated octahedrons (b-cage) at eight corners of a cube and each edge of the cube is formed by joining two b-cages. Each b-cage encloses a cavity with a free diameter of 0.66 nm and each unit cell encloses a larger cavity (a-cage). There are two interconnecting, three-dimensional channels in zeolite HS: (i) connected a-cages, separated by 0.3 nm apertures, (ii) b-cages, alternating with a-cages separated by 0.22 nm apertures. Thus, molecules smaller than 0.3 nm in diameter can diffuse easily through the nanopores of the zeolite. In addition, position of sodium ions in unit cells is important since these ions act as the sites for water sorption and transport through the membrane. For a typical zeolite, a unit cell having the composition $Na_6[Al_6Si_6O_{24}](OH)_2.(1.5\ H_2O)$, eight (out of 12) sodium ions are located inside an a-cage and four ions are located in b-cages. Transport of solvent species (mainly water) through the zeolite matrix comprises of three steps: (i) strong adsorption of the species into a cage from feed side, (ii) surface diffusion of the species from cage to cage and (iii) vaporization of the species to permeate side. Normally, any physical adsorption process includes both Vander Waals dispersion-repulsion forces and electrostatic forces comprising of polarization, dipole and quadrupole interactions. However, since the zeolites have an ionic structure, the electrostatic forces become very large in adsorption of polar molecules like H_2O. This effect is manifested in the fact that heat of adsorption of water into zeolitic adsorbents is unusually high (25–30 kcal/mole) (Huang et al., 2006).

There are different methods for the synthesis of zeolite membranes. These include a gel solution is heated to different ways to be synthesized zeolite product. Almost always, zeolites are prepared via hydrothermal synthesis, i.e., using an aqueous gel consisting of sodium hydroxide and a silicon and an aluminum source in an autoclave at temperatures from 363–523 K. Compared with the conventional hydrothermal synthesis method, DGC method allows solid hydrogel transformation of zeolite with high yield, and it involves nearly complete conversion of gel to zeolite. Moreover, the DGC method enables minimization of waste disposal and reduction in reactor volume. The DGC, a new hydrothermal synthesis route performed in the presence of a vapor phase, shows numerous advantages in comparison to the classical hydrothermal method. The synthesis of low silica zeolites from the dry gel method essentially consists of many steps: (i) Thermal activation of the kaolinite in order to get metakaolinite, (ii) Hydrothermal reaction of metakaolinite with various aqueous alkalis medium.

2. Materials and Methods

2.1. Basic process of the synthesis

In DGC method, the gel is used less frequently which is the same amount that is required to form a thin film membranes of primary gel used. That makes more than 99 percent in savings and only about 1% gel from the gel membrane that clings to the base used for the film. Synthesis process using water vapor as follows**:** (1) Seeds of the support, (2) Put a film of gel on the base seeded, (3) Drying of the support gel, (4) Put the support in an autoclave, (5) Use a little of water at the bottom of autoclave to provide steam, and (6) Autoclave for a specified time and temperature put in the oven (Fig. 2).

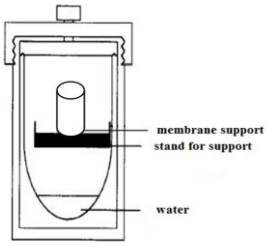

Fig. 2. Scheme of autoclave in dry gel synthesis

2.2. Support preparation

In ceramic membranes, thin dense layers are usually deposited over porous supports. The porous supports provide mechanical strength for the thin selective layers. Porous supports can be made from alumina, cordierite, mullite, silica, spinel, zirconia, other refractory oxides and various oxide mixtures, carbon, sintered metals and silicon carbide. In this research, mullite supports have been prepared from kaolin clay. Kaolin is thermally converted to mullite via high temperature calcinations. The reaction takes place when kaolin is utilized as the sole source of silica and alumina. The reaction can be represented as below:

$$3(Al_2O_3.2SiO_2) \longrightarrow 3Al_2O_3.2SiO_2 + 4SiO_2$$

Free silica ($4SiO_2$) is generated as a result of this conversion. The free silica has been leached out and then porous mullite bodies have been prepared. Mullite has several distinct advantages over other materials. Since kaolin is heated to high temperatures to achieve the mullite conversion reaction, strong inter-crystalline bonds between mullite crystals are formed and this results in excellent strength and attrition. Leaching time depends on several factors including: (1) the quantity of free silica to be removed, (2) the porosity of body prior to leaching, (3) the concentration of leaching solution, and (4) temperature.

Kaolin (SL-KAD grade) has been supplied by WBB cooperation, England. Analysis of the kaolin is listed in Table 1. Cylindrical shaped (tubular) bodies (ID: 10 mm, OD: 14 mm and L: 15 cm) have been conveniently made by extruding a mixture of about 75-67% kaolin and 25-33% distilled water. Suitable calcinations temperatures and periods are those at which kaolin converts to mullite and free silica. Good results have been achieved by calcining for about 3 h at temperatures of about 1250 °C (Speronello 1986a; Speronello 1986b; Sato et al., 2008).

Table 1: Analysis of kaolin clay

Components	Percent (%)	Phases	Percent (%)
SiO_2	51.9	*Kaolinite*	*79*
TiO_2	0.1	*Illite*	*8*
Al_2O_3	34.1	*Quartz*	*10*
Fe_2O_3	1.4	*Feldspar*	*3*
K_2O	0.8	Total	100
Na_2O	0.1		
L.O.I	11.6		
Total	100		

Free silica has been removed from the calcined bodies after leaching by strong alkali solutions. Removal of the silica causes mesoporous tubular supports to be made with very high porosity. Free silica removal has been carried out using aqueous solutions containing 20% by weight NaOH at a temperature of 80 °C for 5 h. Supports have been rinsed using a lot of hot distilled water for a long time in order to remove the all remaining NaOH. Porosity of the supports before leaching is 24.3%, while after treatment it increases to 49%. Flux of the supports before and after free silica removal at 1 bar and 20 °C is 6 kg/m^2h and 10 kg/m^2h, respectively. Porosity of the supports has been measured by water absorption method. Phase identification has been performed by X-ray diffractometry with CuK_α radiation.

2.3. Zeolite membrane synthesis

After preparing the membrane support, zeolite membranes were prepared by the dry gel method.

2.3.1. Coating of the support with seeds

Adding seed crystals to this crystallization system has resulted in increased crystallization rate. The enhanced rate might be due to simply increasing the rate at which solute is integrated into the solid phase from solution due to the increased available surface area, but also might be the result of enhanced nucleation of new crystals. The secondary nucleation mechanism referred to as initial breeding results from microcrystalline dust being washed off seed crystal surfaces in a new synthesis batch. These microcrystalline fragments grow to observable sizes, and result in greatly enhanced crystallization rates due to the increased crystal surface area compared to the unseeded system. Consequently, it is to be expected that addition of seed crystals to a synthesis system will introduce sub-micron sized crystallites into the system, serve as nuclei.

Porous mullite tubes (homemade) as describe above have been used as the support. The external surface of the supports have been polished with 600 grit-sand papers, and then the support has been washed and cleaned with distilled water in a microwave heater for 5 min to remove loose particles created during polishing. Then, supports have been dried at 100 °C for 3h. In order to form a thin and uniform zeolite membrane on the mullite support, the nucleation seeds should be small and uniform in size. In order to inhibit the formation of zeolites into the support pores, the seeds should not penetrate into the pores. Size of the seeds is about 2 μm. The seeds should be dispersed homogeneously on the support surface and the amount of seeds on the support surface should not be too much. Otherwise, the synthesized zeolite membrane is heterogeneous or too thick.

The seeded supports have been prepared by dip-ping the mullite supports in an 8% HS zeolite suspension in a single step. The 8% HS zeolite suspension has been prepared by mixing 8 g HS zeolite in 92 ml distilled water. After dipping procedure, the supports have been dried at 100°C for 3 h (Churl et al., 2010; Churl and Jeong, 2011; Pera-Titus and Mallad, 2006).

2.3.2. Hydroxysodalite zeolite membrane synthe-sis by dry gel method

The dry gel method was used to prepare HS zeolite membranes on porous tubular mullite support (14 mm outer diameter, 12 cm length) with a thickness of 3 mm. The synthesis solution has been prepared by mixing aluminates and silicate solutions. There is source was sodium silicate (Merck, 25-28% SiO_2) and the Al source was sodium aluminates (Aldrich, 50-56% Al_2O_3). Synthesis solution was prepared by mixing aluminates and silicate solutions. NaOH was dissolved in distilled water. The solution was divided into two equal volumes and kept in polypropylene bottles. Aluminates solution was prepared by adding sodium aluminates to one part of the NaOH solution. It was mixed until cleared. Silicate solution was prepared by adding sodium silicate to another part of the NaOH solution. Silicate solution was then poured into aluminates solution and well mixed until a thick homogenized gel was formed. Molar composition of the starting gel of the HS zeolite membranes was $SiO_2/Al_2O_3=1$, $Na_2O/Al_2O_3=65$ and $H_2O/Al_2O_3=1000$.

Two ends of the support have been closed with rubber caps to avoid any precipitation of zeolite crystals on the internal surface of the support during membrane synthesis. The seeded supports are dip in the zeolite gel in the three steps. After dipping procedure, the supports have been dried at 100°C for 3 h. A few cubic centimeters of water carefully poured in the autoclave. The support include gel has been placed vertically in a Teflon autoclave then the autoclave has been sealed. The crystallization has been carried out in an oven at a temperature of 100 °C for 12-24 h. Then, the sample has been taken and the synthesized membranes have been washed several times with distilled water. The pH of the washings solution must be 7. Then, the samples have been dried in air at room temperature for 12 h.

The zeolite membranes were used for dehydration of aqueous ethanol. The ethanol mixtures (90 wt%) were used and experiments were carried out at room temperature (25 °C) within a period of 30-60 min. Permeate concentrations were measured using GC (TCD detector, Varian 3400, carrier gas: hydrogen, column is polyethylene glycol, sample size: 5 micron, column and detector temperatures: 120 °C-150 °C, detector flow rate: 15 ml/min, carrier flow: 5 ml/min, column pressure: 1.6 kPa, GC input pressure: 20 kPa). Performance of PV was evaluated using values of total flux (kg/m^2.h) and separation factor (dimensionless).

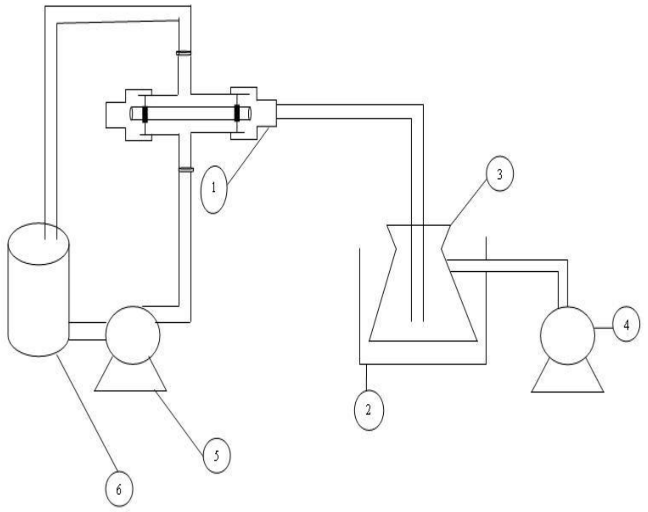

Fig. 3. PV setup: (1) feed container and PV cell, (2) liquid nitrogen trap, (3) permeate container, (4) three-stage vacuum pump, (5) centrifuge pump, (6) feed tank

2.4. Membrane test experiments

2.4.1. Pervaporation tests

The zeolite membranes have been used for long-term dehydration of ethanol. The experiments have been carried out at a temperature of 30 °C and a pressure of 1.5 mbar at the permeate side, within a period of 30-60 min. The pervaporation setup is presented in Fig. 3. Any change of feed concentration due to permeation is negligible because the amount of permeate is small (max 2 ml) compared to total feed volume in the system (0.5 lit). A three stage diaphragm vacuum pump (vacuum brand, GMBH, Germany) has been employed to evacuate the permeate side of the membrane to a pressure of approximately 1.5 mbar while the feed side has been kept at room pressure. The permeate side has been connected to a liquid nitrogen trap via a hose to condense the permeate (vapor). Permeate concentrations have been measured by a GC (TCD detector, Varian 3400). Performance of PV is usually evaluated by total flux (kg/m^{2}h) and separation factor (dimensionless). Separation factor of any organic aqueous solution can be calculated from the following equation:

$$Separation\ factor\ (\alpha) = \frac{\left[X_{H_2O} / X_{Organic} \right]_{permeate}}{\left[X_{H_2O} / X_{Organic} \right]_{feed}}$$

Where X_{H_2O} and $X_{organic}$ are weight fractions of water and organic compound, respectively (Li et al., 2007; Kondo and Kita, 2010, Joaquin et al., 2010; Sorenson et al., 2011).

2.4.2. H_2 and CH_4 permeation

Considering the pore size and the hydrophilic nature of the HS zeolite membrane, this can be nominated for H_2/CH_4 separation. The ideal selectivity can be calculated using the permeabilities. Because the kinetic diameter of CH_4 (0.38 nm) is larger than the pore size of the HS zeolite channels (0.28 nm), only H_2 molecules (2.6 nm) can permeate through a defect-free HS zeolite mem brane. Permeability through the membrane was 4.76 ×10^{-6} mol/Pa.m^2.sec, almost 10 times the amount reported in the literature.

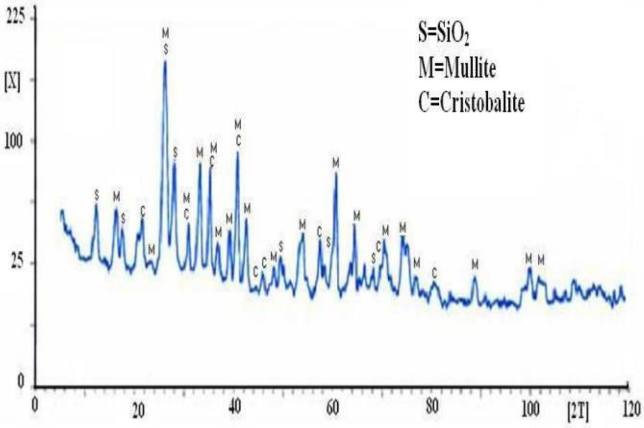

Fig. 4. XRD of the support

3. Results and Discussion

The phases Mullite, Cristobalite and SiO_2 identification was performed by XRD (Philips PW1710, Philips Co., Netherlands) with CuKα radiation. Morphology of the support and the membrane was examined by SEM (JEM-1200 or JEM-5600LV equipped with an Oxford ISIS-300 X-ray disperse spectroscopy (EDS)). Fig. 4 and 5 show XRD patterns of the mullite support and HS zeolite membrane. The XRD pattern of HS zeolite membrane confirms that zeolite HS crystals were formed. Fig. 6, 7 and 8 show SEM photographs of the support surface and the zeolite HS membrane (surface and cross section). Porous structure of the support and thin layer of the membrane can be easily observed.

Table 2. PV performance of HS zeolite membrane was preparated by dry gel method

Sample	**SiO_2/ Al_2O_3**	**Na_2O/ Al_2O_3**	**H_2O/ Al_2O_3**	**t (h)**	**T (°C)**	**Ethanol (%)**	**Flux $kg/m^2.h$**	**Separation factor**
1	1.0	65	1000	12	100	90	0.681	>10000
2	1.0	65	1000	18	100	90	0.750	>10000
3	1.0	65	1000	24	100	90	2.05	>10000

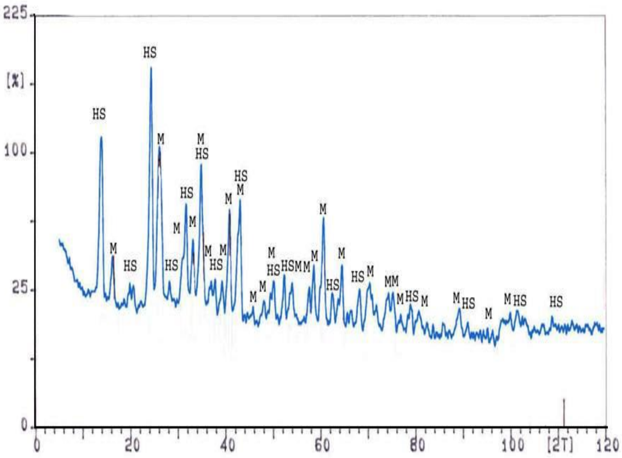

Fig. 5. XRD of the HS zeolite membrane

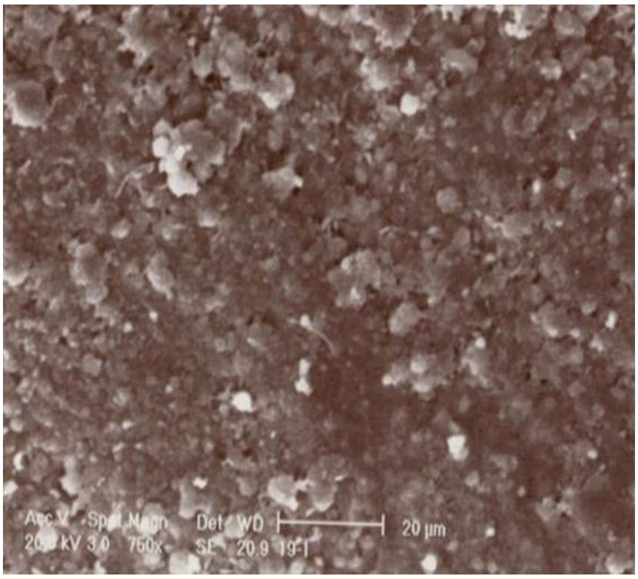

Fig. 6. SEM micrograph of the support

Fig. 7. SEM micrograph of the membrane

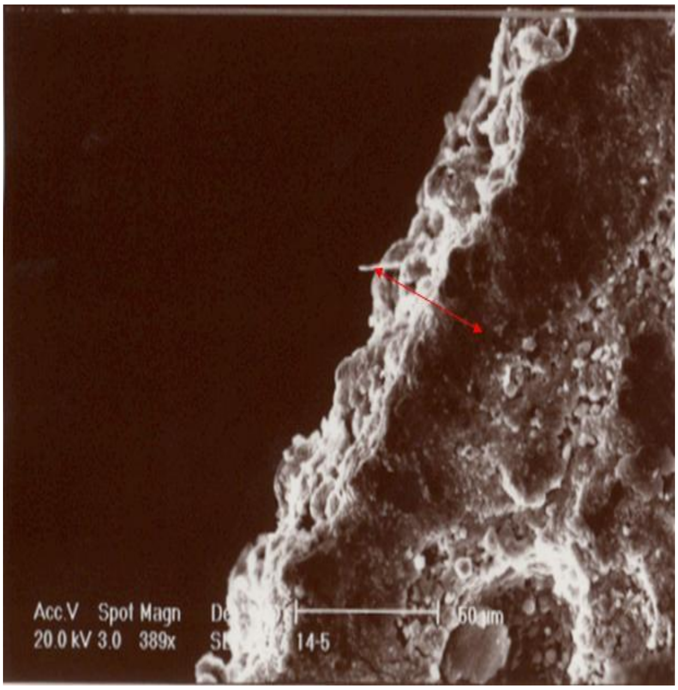

Fig. 8. SEM micrograph of the thickness of membrane on support

Separation performance of the HS membranes was evaluated using pervaporation of ethanol/water mixtures. The HS membrane is highly selective for permeating water preferentially with the high permeation flux because of the micropore filling of water in the zeolite pores and/or the intercrystalline pores between zeolite crystals to afford water-selective permeation through the membrane. The performance of HS zeolite membrane is the most favorable one among PV membranes that have been published so far and is very high enough to put these membranes into industrial applications. As sown in Table 2; the pervaporation performance of HS zeolite membrane formation by dry gel method confirms that dry gel is a cheap method for making HS zeolite membranes.

4. Conclusion

Nano HS zeolite membrane was firstly having been preparated by dry gel method and used for dehydration of aqueous ethanol mixtures. These membranes showed very good membrane performance for separation of ethanol/water mixtures. It is expected that pervaporation using these membranes can be a highly interesting tool for industry, provided they can be produced cheap at a large scale. Separation factors as high as 10000 was obtained at 90 wt% ethanol concentration. In addition, they used for hydrogen separation from CH_4 and it showed high selectivity and permeability ratio to zeolite membrane preparated by conventional method.

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Conflict of interest: Non declare