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PREPARATION OF NANO PORE MORDENITE MEMBRANES

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Abstract: *Nano pore Mordenite membranes were prepared on the outer surface of ceramic tubular tubes via hydrothermal synthesis and evaluated for dehydration pervaporation of water unsymmetrical dimethylhydrazine UDMH mixtures. Highly water-selective mordenite membranes were prepared and the optimum reaction condition was found to be 24 h crystallization time and 170 °C crystallization temperature. Effect of gel composition on separation factor and water flux of the water-UDMH mixtures was investigated. X-ray diffraction (XRD) patterns showed that mordenite is the only zeolite material which presents in the membrane. Morphology of the supports subjected to crystallization was characterized by Scanning electron microscopy (SEM). In PV of the water-UDMH mixtures, the membrane exhibits a hydrophilic behavior, with a high selectivity towards water and a good flux. The best membranes had a water flux of 2.67 kg/m^2.h at 27 °C. The best PV selectivity was obtained to be 264.*

Keywords: *Nano pore Zeolite membrane; Mordenite; Pervaporation; UDMH; hydrothermal synthesis*

1. INTRODUCTION

PV is an economical separation technique compared to conventional separation methods such as distillation especially in processes involving azeotropes, isomers and removal or recovery of trace substances. Due to its high separation efficiency and flux rate, PV results in energy cost saving and safe operation.

Removal of organic compounds from aqueous solutions is important for the recovery of valuable organic products, for the recycling of process water and for the treatment of waste water. Generally, distillation can be used to remove organic compounds from water. However, for low organic concentrations or thermally sensitive organic compounds, distillation is neither economical nor suitable. Furthermore, according to Fleming and alter, PV has several advantages over traditional distillation: (1) reduced energy demand because only a fraction of the liquid that needs to be separated is vaporized, (2) simple equipment since only a vacuum pump is used to create the required driving force and (3) lower capital cost. Thus, relatively mild operational conditions and high effectiveness make PV an appropriate technique for such separations. Most PV studies have been recently focused on dehydration of organic mixtures. In PV, the feed mixture is contacted with a nonporous perm selective membrane. Separation is, in general, explained by the steps of sorption into, diffusion through and desorption from the membrane. The latter is usually considered to be fast and taking place at equilibrium, while diffusion is kinetically controlled and the slowest step of the process. Permeation is dependent on sorption and diffusion steps. The driving force for the separation is created by maintaining a pressure lower than the saturation pressure on the permeate side of the membrane. The mechanism of separation is usually explained in terms of sorption-diffusion processes [1].

UDMH is an important liquid propellant; however it also finds many new applications as an oxygen scavenger for boiler-feed water, a starting material for drug and dye intermediates, a catalyst for polymerization reactions, etc [2- 6].

Membrane-based PV technology has all the requirements for completely replacing extractive distillation for separation of the azeotropes. This can be combined with simple distillation as a hybrid process for enrichment of UDMH to high purity levels. Dehydration of hydrazine and monomethylhydrazine (MMH) using ethyl cellulose membranes have been previously carried out. However, ethyl cellulose can not be used to dehydrate UDMH because it is degraded rapidly. Also, hydrophobic polymers such as poly (dimethelsiloxane) (PDMS) can not withstand the highly alkaline (pH=13-14) medium whereas membranes made of polyethylene and polypropylene give negligible flux so that UDMH can not be selectively extracted from its dilute reaction liquor. The problem of chemical compatibility is also encountered in the case of hydrophilic polymers such as poly (vinyl alcohol) and poly (acrylic acid) [3- 5].

Chitosan, a derivative of the naturally abundant biopolymer chitin, is fully stable in anhydrous UDMH and hence can be selected for its dehydration, keeping in minds its highly hydrophilic nature and good mechanical strength. The promising potential of chitosan as a PV membrane has already been exploited for dehydration of alcohols such as ethanol and isopropanol. This polymer has recently been used to form selective and permeable blend membranes with poly (vinyl alcohol), sodium alginate, etc. However, unfortunately polymeric membranes behaved unsuitable in terms of selectivity and flux in general for water-UDMH mixtures (selectivity and flux of about 10 and 0.01 kg/m^2.h, respectively) [7- 10].

There has been an increasing interest towards zeolite membranes due to their strong potential in separation of liquid mixtures by PV. Zeolite membranes can be prepared with different methods: in situ hydrothermal synthesis; chemical vapor phase method, spray seed coating, etc. Whatever the method, an inorganic porous support is required and its nature and structure may affect the quality of the composite zeolite membrane. A popular support is made of sintered alumina. Nevertheless, this support is expensive and makes the membranes uneconomical. It is thus important to study the possibility of obtaining membranes with cheep supports. Considering its abundant resource, its low cost and its easy processing into a support with a regular structure by sintering; kaolin is a good candidate for the zeolite membranes. Dehydration of organic solvents is presently the major market of PV. Zeolite NaA membranes were reported to be excellent materials for solvent dehydration by PV. But under slightly harsh conditions and under hydrothermal stresses, zeolite NaA membranes turn out to be unstable due to hydrolysis. There are only a few attempts to develop hydrophilic highly siliceous zeolite membranes of different Si/Al ratios with improved hydrothermal stabilities [11- 15].

Since stability of the zeolites in the harsh environments enhances with its silica content, in this paper, preparation method of the hydrophilic mordenite zeolite membrane on mullite support is reported. Performance of the membrane prepared by hydrothermal in situ crystallization was studied for separation of the water–UDMH mixtures by PV through the membrane nano-pores.

2. EXPERIMENTAL

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 were prepared from kaolin clay. Kaolin clay is thermally converted to mullite via high temperature calcinations. The mullitization reaction takes place when kaolin clay is utilized as the sole source of silica and alumina. The kaolin material used in this study (SL-KAD grade) was obtained from WBB cooperation. UDMH (98%) and Sodium hydroxide (Merck) were also used in all experiments. Cylindrical shaped (tubular) bodies (ID: 10 mm, OD: 14 mm and L: 15 cm) were conveniently made by extruding a mixture of about 67-75% kaolin clay and 25-33% distilled water using an extruder. Suitable calcinations temperatures and periods are those at which the clay converts to mullite and free silica. Good results were achieved by calcining for about 3 h at a temperature of about 1250 °C. Support preparation method was published in details elsewhere [16].

The mordenite zeolite membranes were synthesized on the outer surface of the porous mullite tubes. The Si source was sodium silicate

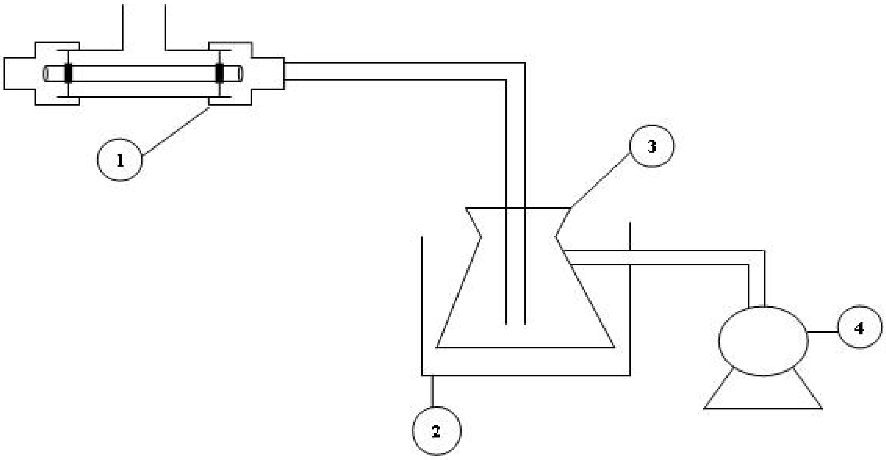

Fig. 1. PV setup; 1- feed container and PV cell 2- liquid nitrogen trap 3- permeate container 4- three stage vacuum pump

and the Al source was sodium aluminate. Synthesis solution was prepared by mixing aluminate and silicate solutions. NaOH was dissolved in distilled water. The solution was divided into two equal volumes and kept in polypropylene bottles. Aluminate solution was prepared by adding sodium aluminate 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 aluminate solution and well mixed until a thick homogenized gel was formed. Molar composition of the starting gel of the mordenite zeolite membranes was SiO_2/Al_2O_3=9–30, Na_2O/SiO_2=9.75, H_2O/Na_2O=780.

For membrane preparation, two ends of the supports were closed with rubber caps to avoid any precipitation of the zeolite crystals on the inner surface of the supports during membrane synthesis. The seeded supports were placed vertically in a Teflon autoclave. The solution was carefully poured into the autoclave and then the autoclave was sealed. Crystallization was carried out in an oven at a temperature of 170 °C for 24 h. Then, the samples were taken and the synthesized membranes were washed several times with distilled water. The samples were then dried at room temperature in air and then dried in the oven at 100 °C for 15 h prior to characterization and evaluation [17, 18].

The zeolite membranes were used for dehydration of water UDMH mixtures. The experiments were carried out at a temperature of 30 °C and a pressure of 1.5 mbara at the permeate side, within a period of 30-60 min.

Permeate concentrations were measured using GC (TCD detector, Varian 3400, carrier gas: hydrogen, column: polyethylene glycol, sample size: 5 μm, column and detector temperatures: 120-150 °C, detector flow: 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). While PV system was at steady state (after 20 min), weight of permeate was measured at 30 min period and then flux was calculated (surface area of the zeolite membrane was 44 cm^2). The change in feed concentration due to permeation was negligible because the amount of permeate was small (max 2 ml) compared with total liquid volume in the system (0.5 lit). A three stage diaphragm vacuum pump (vacuubrand, GMBH, Germany) was employed to evacuate the permeate side of the membrane to a pressure of approximately 1.5 mbara while the feed side was kept at atmospheric pressure. The permeate side was connected to a liquid nitrogen trap via a hose to condense the permeate (vapor) (Figure 1).

Phase identification was performed by XRD (Philips PW1710, Philips Co., Netherlands) with CuKα radiation. Also, morphological studies were performed using SEM (JEM-1200 or JEM-5600LV equipped with an Oxford ISIS-300 X-ray disperse spectroscopy, EDS).

3. RESULTS AND DISCUSSION

It is well known that PV performance of a dense polymeric membrane depends on ability of solvent species to be dissolved in the membrane at its interfaces, and their diffusion into the membrane. When a zeolite membrane is used as separation barrier, the solvent species can not be dissolved in the membrane phase but they are adsorbed on zeolite sites of the inorganic materials. Their adsorbed capacities depend on the affinity of membranes toward the solvents to be removed.

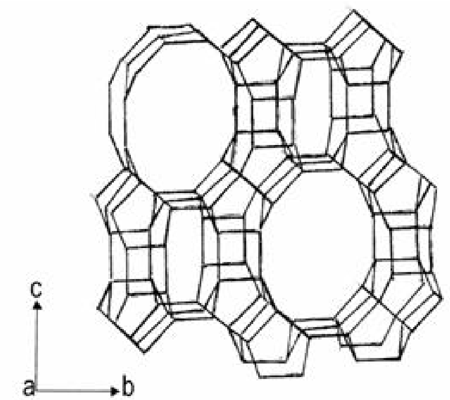

Fig. 2. Schematic representation of mordenite structure

The membrane exhibited a high selectivity towards water in the water-UDMH mixtures. The results show that the permeate water flux reaches to a value as high as 2.67 kg/m^2.h for a UDMH concentration of 5 wt. %. The fact that the membrane has a high selectivity to water clearly indicates that the zeolite layer does not have any through-holes, and the transport is diffusive but not convective. The results also confirm that the mordenite membrane behaves as a hydrophilic membrane, probably due to the presence of polar Al atoms in the zeolite crystal structure. The mordenite zeolite has large channels of 0.67 nm × 0.70 nm and small channels of 0.26 nm × 0.56 nm making the mordenite membrane suitable for

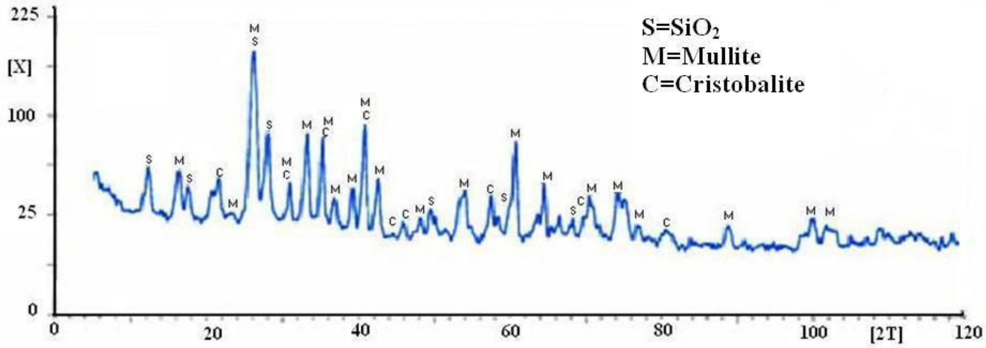

Fig. 3. XRD pattern of the mullite support

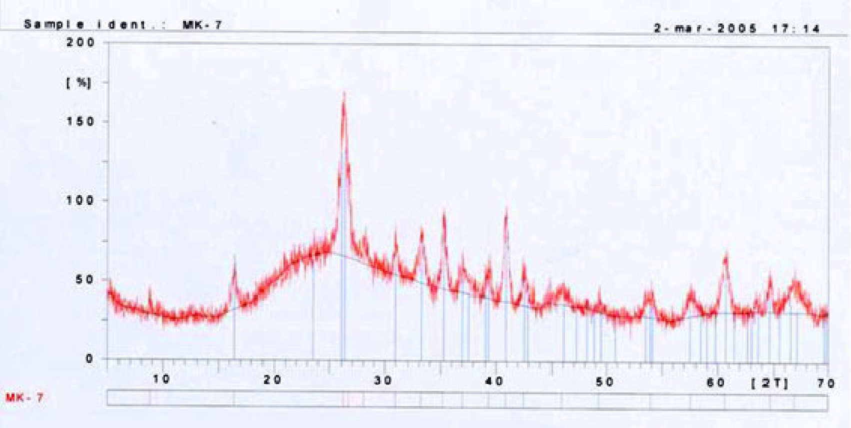

Fig. 4. XRD pattern of the mordenite zeolite membrane

Table 1. Flux and separation factor of the mordenite zeolite membranes

Sample	Na_2O/ Al_2O_3	SiO_2/ Al_2O_3	H_2O/ Al_2O_3	T (h)	T (°C)	UDMH (%)	Flux ($kg/m^2.h$)	Separation factor
1	9.75	30	780	24	170	5	2.67	132
2	9.75	17	780	24	170	5	0.94	198
3	9.75	9	780	24	170	5	2.14	264

removing water from organics.

The mordenite membrane showed a water-UDMH ideal selectivity of 264 at 27 °C, indicating its reasonable quality. Even higher selectivities may be expected for higher quality membranes. The kinetic diameter of water is 0.26 nm. During PV, water permeates through both zeolite and non-zeolite pores because of its higher diffusion rate through the membrane nano-pores.

Figures 3 and 4 show XRD patterns of the mullite support and the mordenite zeolite membrane. Morphology of the support subjected to crystallization was characterized by SEM (Figure 5). Figure 6 shows morphology of the mordenite membrane (surface and cross section). As seen, most of the crystals lie disorderly on the surface. The SEM photograph of the mordenite membrane (cross section) shows that the mullite surface is completely covered by a mordenite crystal layer, whose thickness is larger than 40 μm. The crystal layer is composed of two layers, the top layer consists of pure mordenite crystals and the intermediate one, of mordenite crystals grown in the mullite pores.

As seen in Table 1, the best selectivity was 264 and the best water flux was 2.67kg/m².h at 27 °C. The best membranes were prepared using the following gel molar composition: $9.75Na_2O: 1.0Al_2O_3: 9.0SiO_2 : 780H_2O$. Also, it was found that water separation factor increases with decreasing the SiO_2/Al_2O_3 ratio.

4. CONCLUSION

Nano pore Mordenite membranes were firstly used for dehydration of water-UDMH mixtures. The membranes were synthesized on the outer surface of porous mullite tubes by hydrothermal method. The mullite supports were made by extruding kaolin clay. Zeolite membranes showed much higher fluxes and separation factors than commercially available polymeric membranes. The membranes showed good membrane performance for separation of the

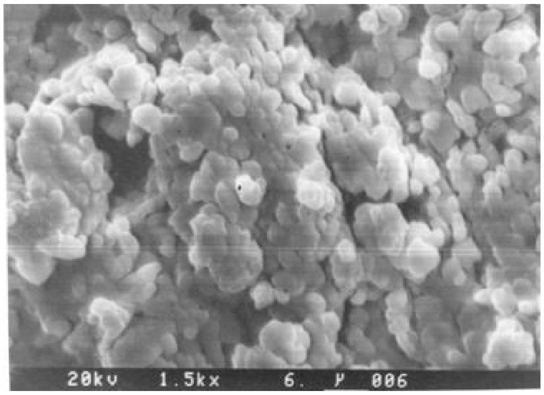

Fig. 5. SEM of the mullite support

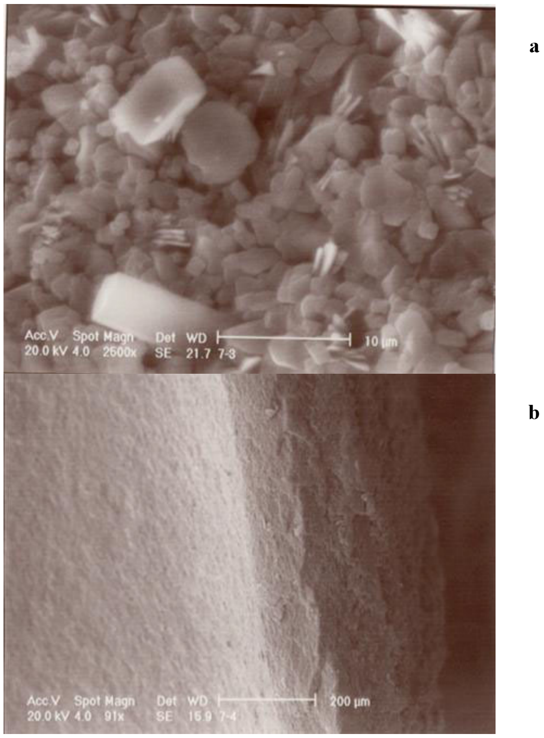

Fig. 6. SEM of the mordenite zeolite membranes a) surface and b) cross section

UDMH-water mixtures. It is expected that even significantly higher fluxes, with similar separation factors, can be achieved at higher temperatures. Since mordenite zeolite membranes can withstand high temperatures and harsh environments (pH>12), dehydration of the water-UDMH mixtures can be performed. It was found that PV using mordenite zeolite membranes is an effective technique to separate water from the water-UDMH mixtures.

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