

Characterization and preparation of porous membranes with a natural Mexican zeolite

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys.: Condens. Matter 16 S2345

(<http://iopscience.iop.org/0953-8984/16/22/037>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 27/05/2010 at 15:17

Please note that [terms and conditions apply](#).

Characterization and preparation of porous membranes with a natural Mexican zeolite

V Pérez Moreno^{1,3}, J J Castro Arellano² and H Balmori Ramírez²

¹ Programa de Ingeniería Molecular, Instituto Mexicano del Petróleo, México DF, CP 07730, Mexico

² Sección de Estudios de Postgrado e Investigación, Escuela Superior de Ingeniería Química e Industrias Extractivas, Instituto Politécnico Nacional, México DF, CP 07738, Mexico

E-mail: vperez@imp.mx

Received 10 October 2003

Published 21 May 2004

Online at stacks.iop.org/JPhysCM/16/S2345

DOI: 10.1088/0953-8984/16/22/037

Abstract

The potential of a natural Mexican zeolite from the northern state of Sonora as microfiltration membranes was evaluated. The zeolite was characterized by x-ray diffraction, scanning electron microscopy (SEM), N₂ physisorption and thermal analysis. Clinoptilolite and heulandite were the main components of the zeolite. The crystallinity of this material was confirmed.

Two steps made up the manufacturing process of porous membranes: pressing and sintering. It was necessary to use lubricants and agglomerants with different particle size of the zeolite. The best properties of the porous membranes were obtained using zinc stearate (4 wt%) as lubricant, boehmite (15 wt%) as agglomerant and the best particle size ranged from 63 to 300 μm . Moreover it was observed that the zeolite granule distribution improved the press of the materials by approximately 10% in the distribution proposed. The thermal treatment of the porous membranes was carried out at several temperatures (500–1000 °C).

The porous membranes obtained were characterized by x-ray diffraction, scanning electron microscopy and N₂ physisorption to study the global porosity, phase transformations and pore size distribution. A loss of crystallinity, decreased porosity and a lower specific surface area were found when the sintering temperature was increased. The results of pore distribution suggest that these materials are porous membranes for microfiltration.

1. Introduction

In the last 30 years, intensive development in a technological process based on the use of membranes has been achieved (Winston *et al* 1994). It is a new inter-disciplinary

³ Author to whom any correspondence should be addressed.

technology with a big field of application: osmosis, electro-osmosis, osmosis inverse, dialysis, electro-dialysis, hemo-dialysis, microfiltration, ultrafiltration, gas separation, pervaporation, distillation of membrane, transportation of liquid membranes and catalytic membranes (Jacangelo *et al* 1998, Der Bruggen *et al* 2003). This process is applied in the following industries: chemical, petro-chemical, biochemical, nuclear and food production (Hwang 1982). Membrane processes have excellent separation capabilities and show promise for meeting many of the existing and anticipated drinking water standards (Lahlou 2000). Membrane technology is a promising alternative to conventional water treatment. Membranes can remove turbidity, bacteria and another microorganisms, and the organic compounds responsible for colour and trihalomethane. Membranes can soften water. They can transform brackish water and even seawater into drinking water by removing the dissolved salts, a capability not shared by conventional treatments (Jacangelo *et al* 1989).

The problem in this process is the preparation of inorganic porous membranes, considering some of the advantages in comparison with polymers and another material as: thermal stability, physicochemical stability without the problems of pressing or dilation, resistance to chemical and micro-biologic attacks, and the possibility of retro-washing and/or sterilization (Hsieh 1984, Strathmann 2001).

Concerning the properties of the natural Mexican zeolites, this material was considered as prime material for the development of porous membranes, due to the fact that in the literature the ability of these materials to become agglomerate has been previously reported in general for other zeolites (García 1993). For the development of porous membranes, the main purposes were to create a structure with a good porous homogeneous distribution, to obtain good physicochemical stability, to define the porosity in order to allow the selective separation of a mixture and to obtain a high permeability.

Currently, these aspects have not been studied yet using this natural zeolite, despite the fact that in northern Mexico this material is abundant and so potentially available to be used in the development of very cheap microfiltration membranes.

2. Experimental details

The starting material was a natural Mexican zeolite from Sonora, Mexico. The physical and chemical properties of the natural Mexican zeolite were determined, the composition and crystalline structure being determined by means of x-ray diffraction (Diffractometer Shimadzu XD-3A using a tube with Cu anode and Ni filter) and transmission electron microscopy (JEOL Microscope model JEM-2000 FXII). The specific surface area and diameter of pore were determined by means of the N₂ physisorption (Micromeritics model ASAP-2000) method and the transformation of phases and thermal stability were determined by thermal analysis.

First the natural Mexican zeolite was crushed and screened. The technique for the preparation of membranes developed in this work was by pressing of the prime material and later the membrane was treated thermally to obtain the final membrane. During the pressing of the raw material, it was necessary to consider additives, choosing adequate lubricants (3–5 wt% for each material): graphite, polyvinyl alcohol, stearic acid and zinc stearate, and also adequate agglomerants (9–18 wt% for each material): kaolin and boehmite. Another parameter considered was the influence of the zeolite granule (to obtain an adequate pressing, gross particles and fine particles were used to eliminate the macro-porosity) in the range from 63 to 300 μm . The different pressings used were uniaxial (2–8 tons) or isostatic (20–40 kg cm⁻²). After pressing the membrane was treated at thermal temperature (500–1000 °C) to strengthen the material and to obtain the final membrane. The siliceous materials usually produce glass during the operation of sintering and reduce the porosity of the material (Vanvlack 1973).

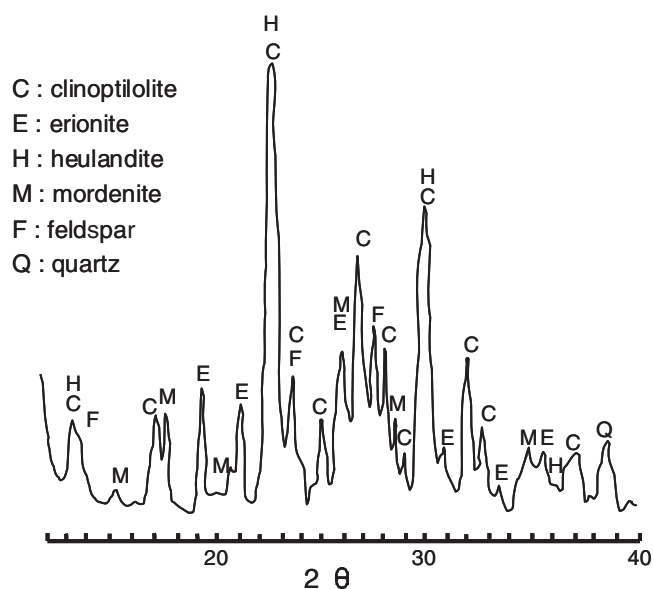


Figure 1. Composition and crystalline structure of the natural Mexican zeolite being determined by means of x-ray diffraction.

The physical and chemical properties of the obtained membranes were also determined; the crystalline structure being determined by means of x-ray diffraction, the global porosity was determined by scanning electron microscopy and the pore size distribution by N_2 physisorption.

3. Results and discussion

3.1. Characterization of raw material

In figure 1, the x-ray diffraction pattern of the natural zeolite is presented showing that the peaks of major intensity corresponded to clinoptilolite and heulandite. Other species are present in minor proportions such as erionite and mordenite; also this material contains feldspar and quartz. In relation to these results, a preliminary report by Maubert *et al* (1984), estimated that this material contained 95% of zeolite and the remainder other materials, an estimate of 70–85% of clinoptilolite.

Using SEM we found that the size of the crystals of the natural zeolite was in the range 200–500 nm and the form was crystalline stony-like.

Using the BET method (N_2 physisorption) the specific surface area of the natural zeolite was determined, being $16 \text{ m}^2 \text{ g}^{-1}$; this value coincides with the value reported by Maubert *et al* (1984) corresponding to the specific surface area for the zeolite containing, principally, clinoptilolite. By this method the diameter of the pore was determined to be near 200 Å and the total volume of pores was found to be $0.047 \text{ cm}^3 \text{ g}^{-1}$. By atomic absorption the ratio Si/Al was determined to be Si = 6.59% and Al = 22.53%.

The thermal gravimeter analysis (TG) and thermal differential analysis (DTA) of the studied natural zeolite is shown in figure 2.

This figure shows four endothermic reactions. The first peak at 140 °C is due to dehydration of zeolite, eliminating the superficial water contained in the zeolite. The reaction at 260 °C could be due to an existing transformation to obtain normal heulandite to heulandite B reported

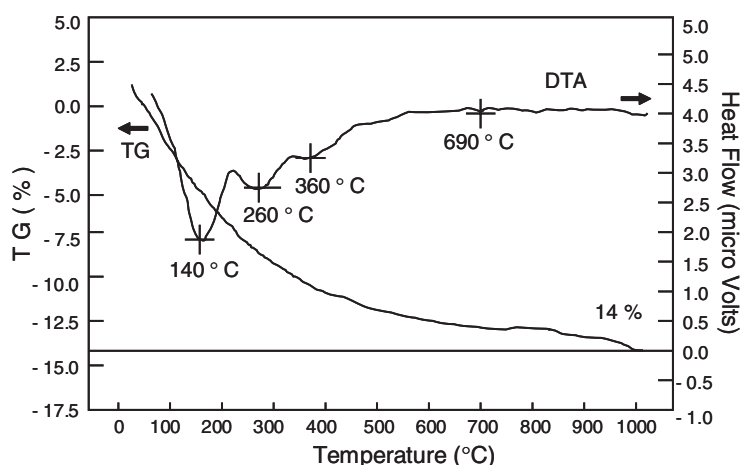


Figure 2. Phase transformations and thermal stability of the natural zeolite determined by thermal analysis.

by Ríos and Badilla (1978). At 360 °C another reaction was observed due to slow structural water elimination of the zeolite. And finally, at 690 °C we observed a small reaction due to the structural change of clinoptilolite, reported in the literature close to 700 °C (Breck 1974).

By thermal gravimeter analysis (TG) of the natural zeolite the total weight loss of the zeolite was shown, mainly due to the loss of superficial and structural water contained in the zeolite; 14% of total weight was lost in the range of 23–1000 °C.

The value of total weight loss of raw material is 14% coinciding with the theory calculation, and this corresponds to the molecules of water contained in the chemical formula ($\cong 15\%$ for different species: clinoptilolite = $\text{Na}_6((\text{AlO}_2)_6(\text{SiO}_2)_{30}) \cdot 24\text{H}_2\text{O}$, heulandite = $\text{Ca}_4((\text{AlO}_2)_8(\text{SiO}_2)_{28}) \cdot 24\text{H}_2\text{O}$, erionite = $\text{Ca}_{4.5}((\text{AlO}_2)_9(\text{SiO}_2)_{27}) \cdot 27\text{H}_2\text{O}$ and mordenite = $\text{Na}_8((\text{AlO}_2)_8(\text{SiO}_2)_{40}) \cdot 24\text{H}_2\text{O}$).

3.2. Method of preparation of porous membranes

The technique for the preparation of the membranes developed in this work was by pressing of the raw material and later the membrane was treated at thermal temperatures to give resistance to the material and to obtain the final membrane. First the natural Mexican zeolite was crushed and screened. During the pressing of the raw material (natural zeolite) it was necessary to consider additives, choosing adequate lubricants (graphite, polyvinyl alcohol, stearic acid and zinc stearate). When graphite and polyvinyl alcohol were used, the membranes break easily. However, when stearic acid and zinc stearate were used the obtained membranes were successful. For stearic acid and zinc stearate in combination with the zeolite, the global density was determined against the uniaxial pressure and the best properties were found for the zinc stearate (4 wt%). For the agglomerants, with the kaolin, the membranes were crushed after sintering. The best properties for obtaining the membranes (membranes without problems of rupture) were found using boehmite (15%), and taking into consideration the influence of the zeolite granule. In the range from 63 to 300 μm of size particles, a package model of particles was applied, as described by Andresson and modified by Dinger and Funk (1982), in order to know the influence of the zeolite granule during the preparation of the membranes. According to the theory of these authors, the simultaneous introduction of particles of maximum and

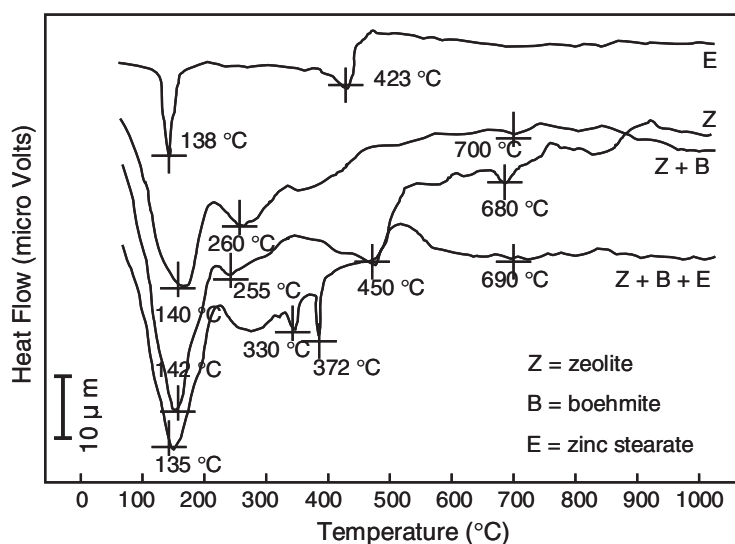


Figure 3. Phase transformations of a natural zeolite without and with additives (zinc stearate and boehmite) determined by thermal analysis.

minimum sizes originates causes the small particles to come in contact with the big particles and fill the empty spaces, and hence reduce porosity.

3.3. Thermal analysis of mixtures

The natural zeolite with the additives (zinc stearate and boehmite) was characterized by thermal gravimeter analysis to be compared with the natural zeolite. In figure 3 two reactions are determined for the zinc stearate (E), first an endothermic reaction at 138 °C due to the fusion of material, then later at 423 °C the combustion of organic material with only the ZnO present is shown. When the zeolite is mixed with the boehmite (Z + B) a reaction is shown at 140 °C, due to the dehydration of both materials; at 255 °C another reaction was observed coinciding with the natural zeolite due to the phase change of heulandite to heulandite B. At 450 °C a strong change originating in the transformation suffered by the boehmite causes a change at gamma- Al_2O_3 to be observed. The last change manifested at 680 °C is caused by the structural change of the species clinoptilolite. For the natural mixture zeolite with zinc stearate and boehmite (Z + B + E) a change is observed at 135 °C due to the water being eliminated in all the materials present and to the fusion of zinc stearate, at 330 °C a strong peak at 372 °C is also observed; these are probably caused by a reaction as a consequence of the mixing of the materials to be sintered. It was observed that the raw material with the additives suffered thermal changes in the range 23–500 °C and later presented an acceptable thermal stability. It is recommendable that work be carried out in the range 500–1000 °C (because the zeolite is more stable) for the preparation of membranes, and up to 1000 °C the structure of the zeolite is destroyed (fusion temperature \approx 1150 °C).

The zeolite with the addition of a lubricant (zinc stearate 4 wt%) and an agglomerant (boehmite 15 wt%) were perfectly mixed to be analysed later by x-ray diffraction (figure 4) and to be compared with the analysis of the original zeolite. The purpose of this comparison was to know if there were any differences between both analyses that can alter the properties of these components. For this analysis very small attenuation was observed in some peaks

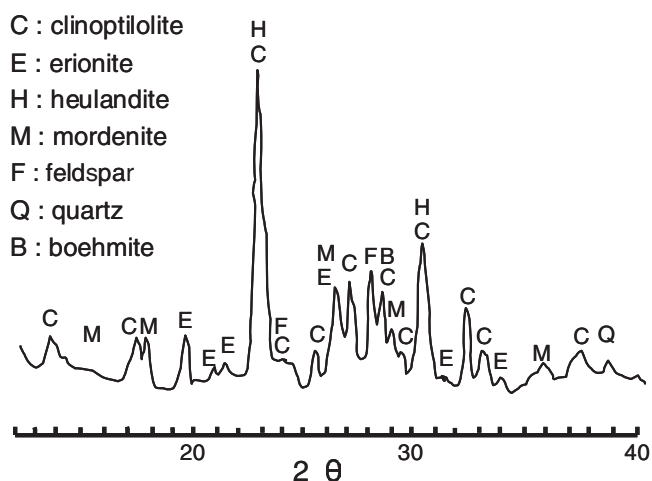


Figure 4. Crystalline structure of the natural zeolite with additives (zinc stearate and boehmite) determined by x-ray diffraction.

in the mixture due to the decrease of the total content of zeolite, being of around 80% in the mixture.

In figure 5 the changes for the membranes obtained are shown; at 25 °C the peaks are acute and numerous which is characteristics of a crystalline material. Between 25 and 500 °C, the disappearance of diverse species was observed: mordenite, feldspar, quartz, boehmite and the other peaks of major intensity have a little attenuation. The existing changes between 500 and 700 °C are remarkable, the peaks characteristic of the zeolite disappear completely. At 1000 °C the peak characteristic of zeolite does not exist; the existing peaks are small, the biggest one corresponds perhaps to silicate of sodium hydrate, which corresponds to the destruction of the original crystalline structure of zeolite.

The presses used were uniaxial (2–8 tons) and isostatic (20–40 kg cm⁻²). Because of the complexity of the design, a cylindrical membrane by isostatic pressing was discarded. For uniaxial pressing the best result was at 8 tons, because at this value a high global density with less porosity was found.

3.4. Characterization of membranes

In the membrane press at 8 tons and after sintering at between 500 and 1000 °C and analysis by scanning electron microscopy, an increase in the size of the particles was found, and a decrease in the pore size of around 3000 nm (membrane sintered at 1000 °C, as shown in figure 6).

A N₂ physisorption analysis confirmed in the isothermal curve adsorption and desorption a mesoporous material with an average diameter of pore between 64 and 138 Å. For the membrane sintered at 500 °C a uni-modal distribution of pores was found, with an average diameter of pore determined at 66.2 Å and the specific surface area determined was 45.3 m² g⁻¹. For the membrane sintered at 600 °C a uni-modal distribution of pores was found, with an average diameter of pore determined at 64.2 Å and the specific surface area determined was 45.7 m² g⁻¹. These results are similar to those found at 500 °C, therefore it is supposed that the material does not modify its structure. For the membrane sintered at 1000 °C a narrow uni-modal distribution of pores was found, with an average diameter of pore determined at 138.3 Å and the specific surface area determined was 10.9 m² g⁻¹.

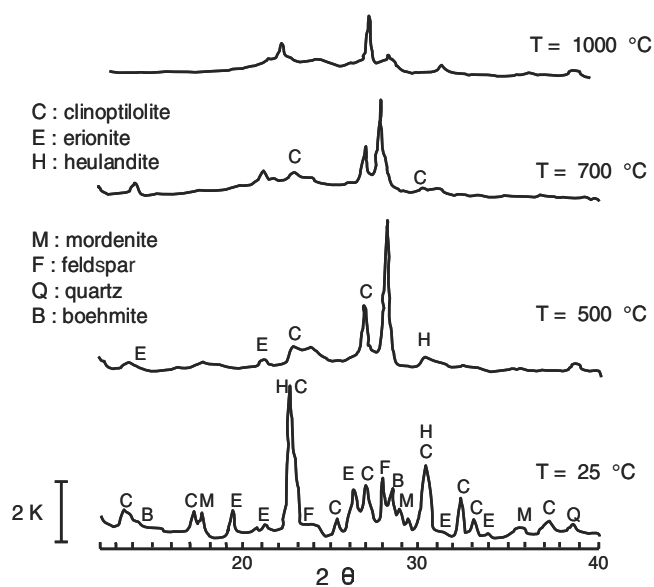


Figure 5. Crystalline structure of the membranes obtained determined by x-ray diffraction.

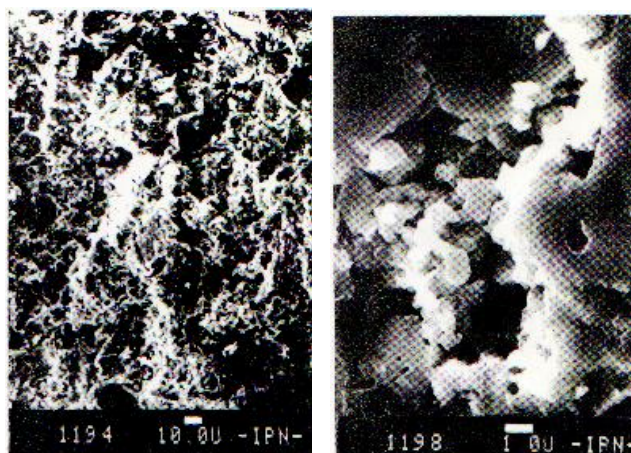


Figure 6. Global porosity of the membranes sintered at 500 °C (left) and 1000 °C (right) determined by scanning electron microscopy.

These results support the idea that these porous membranes have properties to be used in microfiltration processes.

An application of the porous membrane evaluated is the clarification of beer. In a simultaneous experiment the turbidness of lager beer was reduced to 99.5% without affecting other characteristic parameters. Also the copper retention was tested in this porous membrane, obtaining an interchange at about 78%.

4. Conclusions

In the characterization of a natural Mexican zeolite it was determined that the material contains clinoptilolite and heulandite principally, and other species of zeolites such as feldspar and

quartz. The range of temperatures in the thermal stability of this material was also determined, and it was found to be 500–1000 °C. In addition the crystallinity of this material was confirmed.

In the development of porous membranes, it was observed that the additives which produced the best properties were zinc stearate (4 wt%) as lubricant and boehmite (15 wt%) as agglomerant, at the uniaxial pressure of 2–8 tons. The zeolite granule distribution improves the pressing of the materials by approximately 10% in the distribution proposed.

In the characterization of the porous membranes a significant decrease in crystalline structure was observed when there was an increase in temperature, from 500 to 1000 °C, during the sintering treatment. The results of pore distribution support the notion that these materials are mesoporous, which means that the porous membrane obtained in this work is in the range of microfiltration.

In the evaluation of membranes, it is concluded that the porous membranes obtained are membranes that could potentially be used for microfiltration, which can be applied to eliminate, dissolve and suspend solids.

References

- Breck D W 1974 *Zeolite Molecular Sieves* (New York: Wiley) pp 19–35
- Der Bruggen B, Lejon L and Vandecasteele C 2003 Reuse, treatment, and discharge of the concentrate of pressure-driven membrane processes *Environ. Sci. Technol.* **37** 3733
- Dinger D R and Funk J E 1982 Particle packing: review of packing theories *Fine Particle Society, 13th Annual Mtg (Chicago)* pp 87–88
- García P A 1993 Caracterización y comparación de zeolitas naturales mexicanas y sintéticas tipo A *Dissertation Thesis IPN, Mexico DF*, pp 4–15
- Hsieh H P 1984 *Inorganic Membrane, Membrane Materials and Processes (AIChE Symp. Series vol 84)* p 261
- Hwang S-T 1982 Membranes research and applications *J. Sci. Elsevier* **10** 81–3
- Jacangelo J G, Chellam S and Trussell R R 1998 The membrane treatment *Civil Eng.* **68** 42–5
- Jacangelo J G, Patania N and Trussell R R 1989 Membranes in water treatment *Civil Eng.* **59** 68–71
- Lahlou M 2000 Membrane filtration as an alternative: part 1 *Water Eng. Manage.* **147** 12–6
- Maubert M F, Tejero J M, Aguilar A G and Torres R M 1984 Activación de materiales naturales para su aplicación como adsorbentes naturales *Programa de Ciencia y Tecnología para el desarrollo V Centenario México DF* pp 3–10
- Ríos G R and Badilla C R 1978 *Bol. Soc. Geol. Mexicana* **34** 136–45
- Strathmann H 2001 Membrane separation processes: current relevant and future opportunities *AIChE J.* **47** 1077–87
- Vanvlack L H 1973 *Tecnología de Materiales* (Mexico DF: Fondo Interamericano) pp 246–59
- Winston W S, Kamalesh H and Sirkar K 1994 *Membrane Handbook* (New York: Van Nostrand-Reinhold) pp 1–3