PREPARATION OF CERAMIC MEMBRANES FOR MICROFILTRATION BASED ON MARL CLAY AND NATURAL ZEOLITE FROM DEPOSITES IN BULGARIA

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ABSTRACT

The application of ceramic membranes have been increased due to their excellent chemical, thermal and mechanical stability, and high separation efficiency. In the near future, the exploitation of the natural ceramic materials, such as clays, kaolines, zeolites, limestones, and simple fabrication techniques can play a significant role for the preparation of low cost membranes. Natural zeolites are very suitable because of their unique physical-chemical characteristics such as ion-exchange properties and selectivity in sorption. Two-layer ceramic membranes have been produced on the base of porous support prepared from 50 mass % marl clay and 50 mass % natural zeolite and a top layer from natural zeolite from deposits in Eastern Rhodope, which are part of the Rhodope Mountain in Bulgaria. The porous support from 50 mass % marl clay and 50 mass % natural zeolite was molded by semi-dry pressing in disks with diameter 90 mm and thickness 2 mm, and sintered at 900^{o}C. Water absorption, firing shrinkage, apparent density and apparent porosity of the fired support were determined by standard methods for ceramic materials. The top layer applied by dip coating on the fired support was obtained from stable suspension prepared with 8 mass % classified natural zeolite, pure water, 0,75 mass % of defloculant Dolapix P67 and of 1 mass % PVA (Optapix PAF). Dipping time was 1 min. Ceramic membranes were fired at 800^{o}C for 1 hour at a maxumum temperature. The phase composition and the structure of the ceramic support and ceramic membrane were established by XRD and SEM analyses.

Keywords: *ceramic membranes, microfiltration, marl clay, natural zeolite, support, layer.*

INTRODUCTION

The properties of the ceramic membranes are mainly determined by their composition and the sintering temperature. The use of natural raw materials and waste material is certainly preferable than industrial chemicals due to the lower cost and environmental impact. Recently, the development of low cost ceramic membranes based on natural raw materials such as kaolin, clay, zeolite, limestone, dolomite, feldspar, quartz, etc. appeared as an efficient solution for water purification and other liquid media at a low cost [1 - 7]. The applications of ceramic membranes have increased due to their excellent chemical, thermal and mechanical stability, and high separation efficiency. Ceramic membranes with high permeability can only be obtained in a multilayer configuration with a macroporous support, which provides mechanical strength and lowers the flow resistance. The development of naturally mineral-based ceramic membranes can lead to a critical new technological revolution that would add great economic value to natural minerals that exist throughout the world. Natural zeolites have been widely used because of their unique physical-chemical characteristics such as ion-exchange properties and selectivity in sorption. Natural zeolites, are mainly composed of alumosilicates with a three-dimensional framework structure bearing $A1O_4$ and SiO_4 tetraedra. Natural zeolite does not swell in water and easily forms a suspension for coating membranes on a porous support. The multiple compositions of natural zeolites allows their sintering at lower temperature from conventional pure membrane materials. Zeolite membranes have unique pore structures containing two types of pores: uniform sub-nanometer zeolitic pores and intercrystal micropores with certain size distribution [8 - 15].

The aim of this study is to investigate the possibility for obtaining of two layer porous ceramic membranes from marl clay and natural zeolite and characterization of sintered ceramic membranes.

EXPERIMENTAL

Starting materials

The ceramic membranes consist in a ceramic support and a top-layer. The initial raw materials for preparation of the ceramic support for membranes is a marl clay and a natural zeolite from deposits in Eastern Rhodope, Bulgaria. The ceramic support is made from 50 mass % marl clay and 50 mass % natural zeolite. The layer on the support is performed from fine natural zeolite by dip coating. Zeolite containing rocks are situated in the north-easternmost flank of the East Rhodopean Pa-leogene Depression in Bulgaria. Here, medium acid volcanogenic to volcanogenic-sedimentary rock complexes of Oligocene age are cropping out. In the studied region the manifestations of the clinoptilolite zeolitization are most spread.

Preparation of ceramic membranes

For the preparation of the ceramic support, marl clay and natural zeolite are crushed and ground to a fine powders passing through a sieve with mesh size 63 μm. The porous support from 50 mass % marl clay and 50 mass % natural zeolite is molded by semi-dry pressing in disks with diameter 90 mm and thickness 2 mm, then it is sintered at 900°C for 2 hours at maxumum temperature. Zeolite powder for top layer is obtained by wet milling for 5 hours in a planetary mill with rotation speed 200 rpm and dried at 105°C. Then, gravitational sedimentation classification is performed. A suspension with 1 mass % solid loading is left in the specified cylinder to sediment. The top layer for coating of the support, prepared from stable suspension containing 8 mass % classified zeolite, pure water, 0,75 mass % of defloculant Dolapix P67 and of 1 mass % PVA (Optapix PAF) is applied by dip coating on the fired ceramic support. The dipping time is 1 min. Ceramic membranes are fired at 800°C for 1 hour at maxumum temperature, becouse at higher temperature the zeolite can amorphize in thin layer.

Characterization methods

The chemical compositions of the marl clay and natural zeolite are determined by ICP-AES. The mineral compositions of the marl clay and the natural zeolite ars identified by XRD („TUR-M62“, CoKa radiation). The physical-mechanical properties as water absorption, firing shrinkage, apparent density and apparent porosity of fired supports are determined by standard methods for ceramic materials. Porosity of the prepared membrane is evaluated by the Archimedes‘ principle. Phase composition and miccrostructure of the ceramic support is established by XRD analysis. The surface and cross-cection SEM images of the membranes are obtained using scanning electron microscope,‘JEOL JCXL-733 - Japan“.

RESULTS AND DISCUSSION

The chemical composition of the marl clay is presented in Table 1. The marl clay contains 28 wt. % CaO. On Fig. 1 is presented the XRD of marl clay used for the preparation of the ceramic support. The plastic components in the marl clay are montmorillonite and muscovite, with montmorillonite predominating. Non-plastic ones are represented by quartz, plagioclase and calcite.

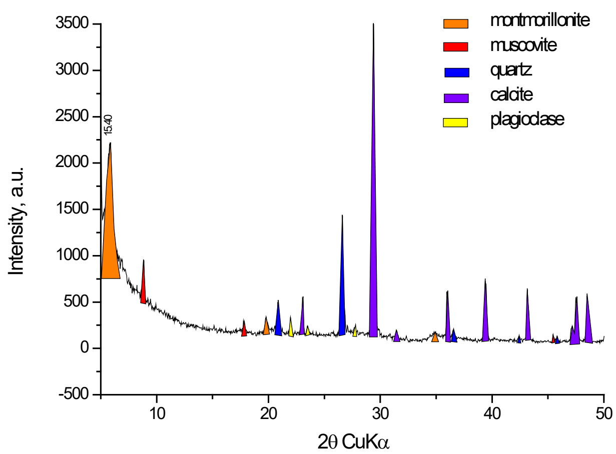

Fig. 1. XRD of the marl clay.

Table 1. Chemical composition of the marl clay.

Oxides	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	K_2O	LOI
Mac. %	33,50	7,50	0.26	2,55	1,40	28,00	0.61	1,77	24,20

Table 2. Chemical composition of the natural zeolite.

Oxides	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	K_2O	LOI
Mass. %	71,35	12,72	0.20	0.90	0.94	2,20	0.94	3,94	12,79

Table 3. Physico-mechanical properties of the ceramic support fired at 900°C and prepared from 50 mass % marl clay and 50 mass % natrual zeolite.

Support composition	Firing shrinkage, %	Water absorption, %	Apparent density, g/cm³	Apparent porosity, %
50 wt.% marl clay and 50 wt. % natural zeolite	5,6	34	1,4	48

The chemical composition of the zeolite powder is shown in Table 2. The major chemical component in the natural zeolite is SiO_2 (71,35 mass %). The content of Fe_2O_3 is very low (0,90 mass %). Besides Al_2O_3 (12,72 mass %) in the zeolite are present also small quantities of CaO, K_2O, Na_2O and MgO. The main component in the natural zeolite is the clinoptillolite (about 83 %). Secondary phases also present in small quantities and an ortoclase and opal - CT. XRD of the natural zeolite is illustrated in Fig. 2.

On Fig. 3 are demonstrated the fired at 900°C ceramic support and the ceramic membrane fired at 800°C. The physical-mechanical properties of ceramic support, sintered at 900°C are presented in Table 3. The porosity of the fired ceramic support (48 %) is suitable for ceramic membranes. The good porosity of the ceramic membranes is the result from pores formed by the decomposition of calcium carbonate during firing and the presence of micropores in the structure of the natural zeolite. Fig. 4 shows the XRD of a ceramic support prepared from 50 mass % marl clay

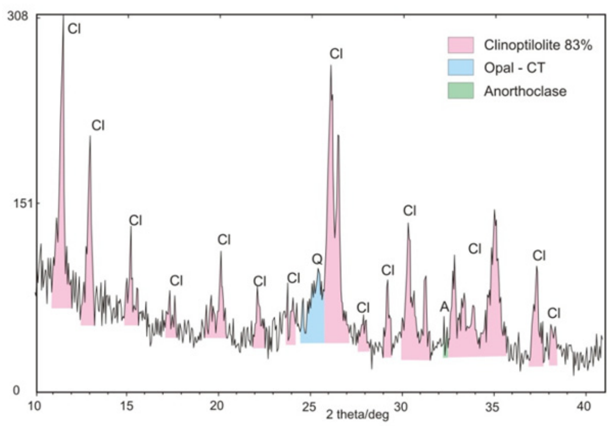

Fig. 2. XRD of the natural zeolite.

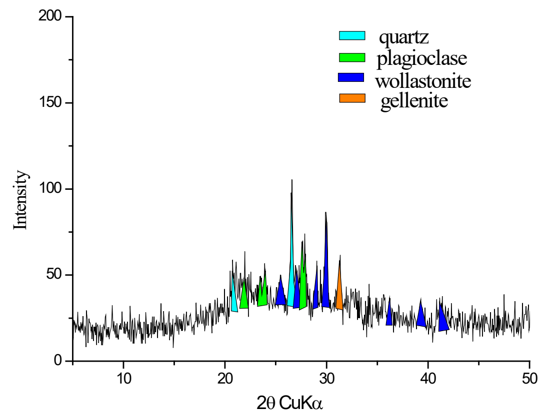

Fig. 4. XRD of ceramic support fired at 900°C.

Fig. 3. Ceramic membrane support, fired at 900°C, and ceramic membrane fired at 800°C.

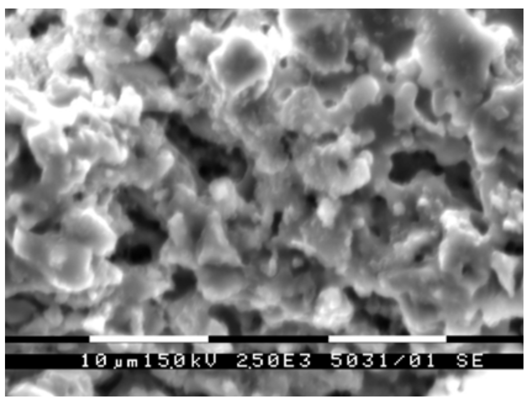

Fig. 5. SEM of ceramic support fired at 900°C.

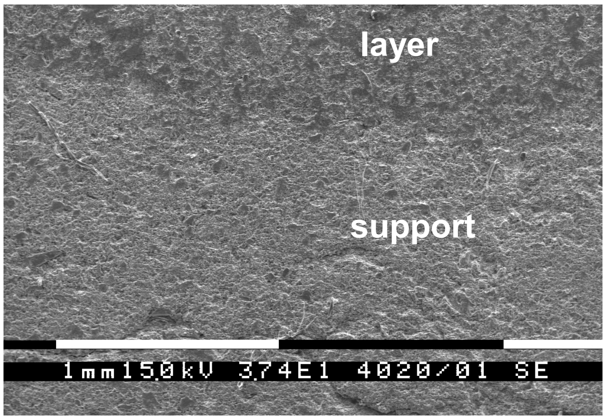

Fig. 6. Cross-section SEM micrograph of two-layer ceramic membrane sintered at 800^{o}C for 1h.

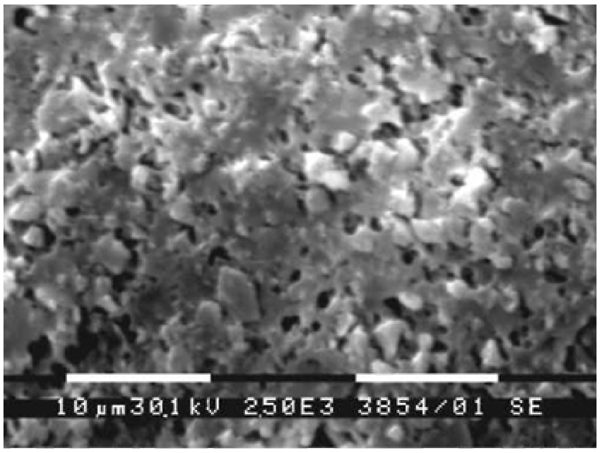

Fig. 7. SEM image of the surface of the ceramic membrane fired at 800^{o}C.

and 50 mass % zeolite, fired at 900°C for 2 hours at maximum temperature. SEM analysis of the same material is given on Fig. 5. The phase composition of the fired at 900^{o}C ceramic support consists in quartz, plagioclase, gellenite and wollastonite. The image shows that the support is with high porosity. The size of the crystals in the support reaches up to 10 mm. The pores size is in the range from 1 to 10 microns.

A cross-section SEM micrograph of sintered at 800^{o}C two-layer ceramic membrane is shown in Fig. 6. It is seen that there are no cracks and the adhesion between the support and top-layer is good. This result confirms that the used suspension has the necessary properties for application by dip coating on the support for ceramic membrane preparation. The membrane surface micrograph illustrated on Fig. 7 indicates that the pore distribution in the membrane is uniform and the pore size in the membrane surface is below 5 um.

CONCLUSIONS

As a result of the research, it can be concluded that the marl clay from deposit in Bulgaria can be applicable for the preparation of low cost ceramic support with good porosity (48 %) for ceramic membranes for microfiltration at low firing temperatures up to 900°C.

Natural zeolite in Bulgaria may find application for obtaining supports and top-layers for low cost multilayer ceramic membranes for microfiltration at low sintering temperature. Before using, the natural zeolite for the top layer has to be subjected to fine grinding and gravitational sedimentation classification of the zeolite powder and sintered at lower temperature (800^{o}C) to ensure high porosity of the ceramic membranes.

The obtained by dip-coating two-layer ceramic membranes are characterized with good adhesion between the support and the top layer, high porosity both of the support and the membrane and a uniform pore distribution.

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