Desalination and Water Treatment
www.deswater.com

doi:10.5004/dwt.2017.20569

76 (2017) 77–82
May

Co-sintered synthesis of needle-like mullite porous membrane materials

Gangling Chen[a,b], Yangyan[b], Youzhi Guo[b,*], Liang Guo[b] , Jianying Zhang[a] , Xiutao Ge[a]

[a]*School of Material Science and Chemical Engineering, Chuzhou University, 239000, China*
[b]*The Seawater Desalination and Utilization of the Alternative Water Resources Research Center of Hohai University, Hohai University, Nanjing 210009, China, Tel. +86-25-58099297, Fax +86-25-58099295, email: gyz57123@126.com (Y. Guo)*

Received 24 October 2016; Accepted 8 January 2017

ABSTRACT

To reduce the production cost and improve the performance of new membranes a high permeability porous mullite membrane material was directly synthesized by designing a mesh structure formed from needle-like mullite. The kaolin powder with 65% Al_2O_3 content served as the precursor material for the porous mullite support, the powder doped 5 wt% AlF_3 with 60% Al_2O_3 content served as the precursor material of the needle like mullite crystal layer. A thin layer of the precursor material of the needle like mullite crystal layer was coated on the support precursor. In the co-sintering preparation of the membrane the free SiO_2 in the kaolin was consumed by the alumina precursors, AlF_3 as additive promoted the formation of mullite whiskers, so that a mesh structure was formed in-situ, which imparted suitable permeability and selectivity to the final structure. The growth of mullite whiskers has a positive impact on the improvement of porosity and permeability of ceramic membranes. The water flux of the membrane increased by 1.2–2 times compared to the existing microporous membranes of the similar pore size. The porosity of the samples was greater than 47% between 1250°C and 1400°C as the sintering temperature was increased. This preparation process simplified the preparation of the bilayer membrane, and greatly decreased the cost of raw material and production time and improved the performance of the membrane product. The bilayer membrane developed in this study may be used as a microfiltration membrane, particularly in high-throughput water treatment applications.

Keywords: Needle-like mullite; Co-sintered synthesis; Ceramic membrane

1. Introduction

Water pollution is one of the most important problems facing modern society, because pure water forms the basis for life. The use of porous ceramic membranes is one of the newest, recently developed techniques for the purification and exploitation of waste water. This approach is an important way to help solve the current water pollution crisis and to help maintain the cleanliness of the environment [1–5]. It has proven its efficiency in the removal of algae, bacteria and viruses from water. In industrial applications, improving the ceramic membrane permeation flux and separation usually requires that the ceramic membranes be a composite type with an asymmetric multi-layer gradient pore structure. Heretofore, alumina has been considered to be the main membrane material for preparing commercial ceramic membranes. However, due to the expense of the raw materials and relatively high firing temperature, production costs have been considered to be too high for some applications [5–9]. This has restricted the use of these membranes from many industrial separations, especially in the area of waste water treatment. At present, the focus of most research in this field has been to reduce the production cost and improve the performance of these membranes [1–4,6,9–11].

The use of mullite in the fabrication of porous membranes has received considerable interest in recent years, because of its unique characteristics including a low thermal expansion coefficient and chemical stability as well as good thermal shock resistance and strength. Much effort has been expended to prepare porous mullite ceramics using a variety of starting materials [9–12]. For exam-

---

*Corresponding author.

ple, kaolin clay has been used since it is an abundantly available mineral in China. The cost of preparing porous membrane material can be significantly reduced if clay minerals are employed as starting materials to directly prepare porous mullite membrane materials. Recently, several researchers have attempted to prepare porous mullite membranes using clay minerals employing a reaction-sintering process. The advantages of this process include simple processing procedures and a relatively low sintering temperature, which make it suitable for large-scale industrial production. One substantial hurdle, however, is the high density of the mullite materials formed in this conventional manner that is caused by the presence of excess SiO_2 in clay. In general, the pores in the membrane are produced by leaching the free silica from fired clays or from the fired product [13–16]. This additional step in the production processing of leaching the silicate is undesirable. Furthermore, the average pore sizes reported for the product resulting from this method were found to be 0.17–0.61 μm. These pore sizes are less than desirable for filtration applications, because they produce low permeability [17–19]. Addition of alumina precursors has been proposed as a possible solution to this problem. The addition of alumina can reduce the amount of the glass phase in the composition and increase the quantity of the mullite. In addition, the generated mullite crystal morphology can be controlled by controlling the composition of the alumina precursor. It is well known that a mesh structure formed from threads or fibers represents the most efficient structure for pressure driven membrane filtration processes. Such structures can achieve high selectivity while maintaining a high flux, because the fibers produce smaller voids without forming dead-end pores and they minimize the reduction in the total void volume [20–23]. The porosity in the separation layer of the nanofibers can be over 70% of its volume. By contrast, the separation layer in conventional ceramic membranes has a porosity of less than 36% and inevitably includes dead-end pores that provide no contribution to the membrane flux.

In this reported investigation, a new processing route was proposed to directly obtain a high permeability, porous mullite membrane material by designing a mesh structure formed from needle-like mullite. This membrane was composed of suitable alumina precursors as the top separation membrane material and the in-situ porous mullite served as a support material. It was expected that the free SiO_2 in the kaolin would be consumed by the added alumina precursors, so that a mesh structure would be formed in-situ, which would impart suitable permeability to the final structure.

2. Experimental procedures

2.1. Sample preparation

The minerals in kaolinite clay ($Al_2O_3 \cdot 2SiO_2$, China Kaolin Company), α-Al_2O_3 and industrial $Al(OH)_3$ powder were used as the starting materials and AlF_3 was used as an additive. The composition of the starting materials was determined by the Switzerland ARL9800XP X-ray fluorescence spectrometer. Two types of starting powders were prepared: kaolin + $Al(OH)_3$, kaolin + α-Al_2O_3 +$Al(OH)_3$ (the amount of α-Al_2O_3 in the additive alumina precursors was 10 wt%), referred to as A and B, respectively. Powder A was doped 5 wt% AlF_3 with 60 wt% Al_2O_3 and was used to fabricate the top-layer membrane (marked A in Fig. 1). Powder B with Al_2O_3 contents of 65% was used to prepare the porous mullite support (marked B in Fig. 1). Mixtures of the starting powders were ball-milled together. The grinding media was corundum balls and the milling time was 12 h. Some binders and lubricants were added to the mixed powder. Schematic illustration of preparation procedure of the ceramic membranes is shown in Fig. 1. A thin layer of the precursor material of the needle like mullite crystal layer was coated on the support precursor. The powder compacts were prepared by a press molding technique. The applied pressure was 8 MPa for 1 min. After drying the molded material was fired at various temperatures ranging from 1250°C to 1400°C for 2 h at the heating rate of 3°C min^{-1} in a programmable electric furnace. The samples were prepared in the temperature programmed furnace and the resultant membranes were labeled "AB". The samples prepared using the precursor materials of the porous mullite support (Powder B) were prepared for comparison and labeled "B".

2.2. Characterization of the samples

The microstructure of sintered samples was examined using scanning electron microscopy (SEM, Quanta 200, FEI, Netherlands) with an energy dispersive X-ray spectrometer (EDX). The crystal phases of the sintered samples were determined by X-ray diffraction (XRD, D8 advance, Bruker

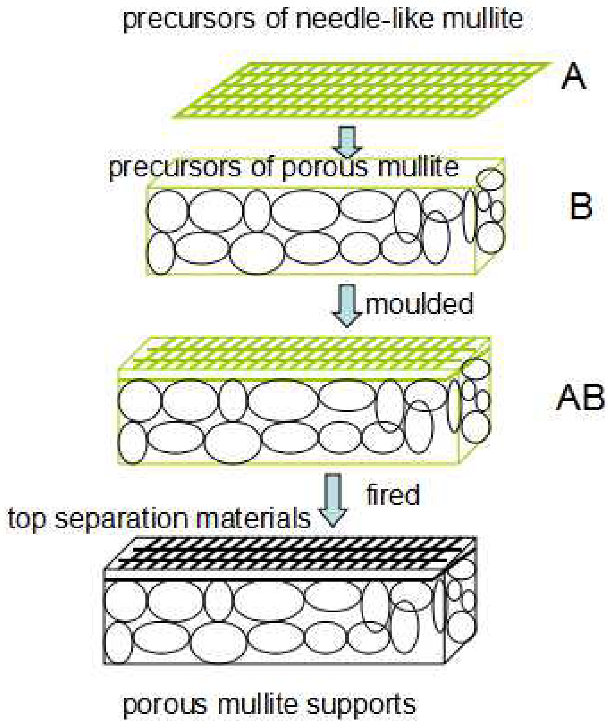


Fig. 1. Schematic illustration of preparation procedure of the ceramic membranes.

Instrument Co., Ltd. Germany). The porosity of the resulting ceramics was determined by the Archimedes method (GB1996-80) with water as the liquid medium. Average pore size of the sintered porous specimens were measured using the gas bubble pressure method (GBP), which was performed using the American Society for Testing and Materials (ASTM) Publication (F316-80). The filtration performance of the samples was characterized using DI water as the medium, and the filtration device used for this testing is shown in Fig. 2. The filtration operating pressure was in the range from 0.1 to 0.3 MPa and each operating pressure produced three sets of data from which the calculated average flow rate was determined that corresponded to the pressure.

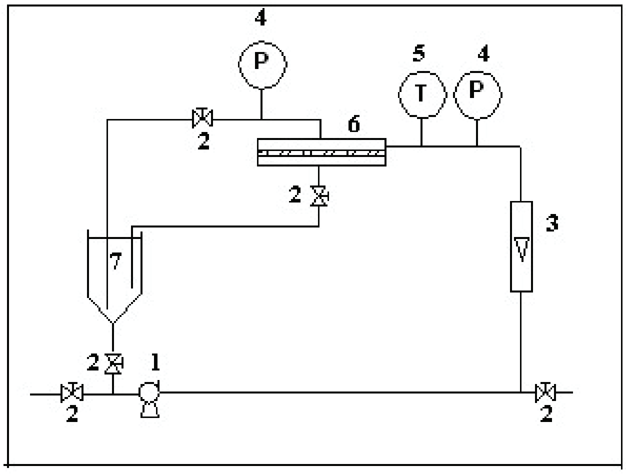
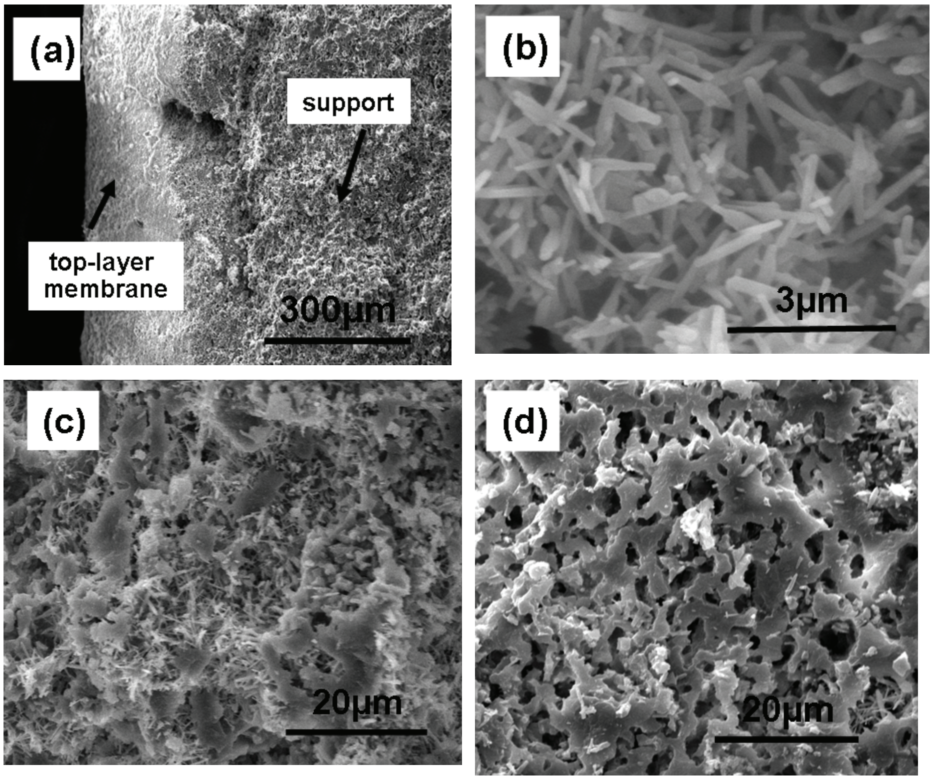


Fig. 2. Schematic diagram of cross-flow filtration experimental equipment: 1 – centrifugal pump; 2 – needle valve; 3 – flow meter; 4 – pressure gauge; 5 – temperature meter; 6 – plate ceramic membrane module; and 7 – stock tank.

3. Results and discussion

3.1. Microstructure of the samples

The SEM photos of produced sample are shown in Fig. 3. It can be seen from this figure that the samples consisted of a two layered structure, which was the top whisker material and porous support containing a suitable pore structure. Among these, the top was prepared by firing the precursor materials of the needle-like mullite crystal layer at high temperature. Fig. 3b shows the top surface of the membrane where a porous network structure is clearly evident. The needle-like mullite crystals touch each other to form a short network and the surface was completely covered by whiskers. The acicular structure of the whiskers appears to have grown randomly to form a porous structure and the average length of each whisker appears to be about 2.5 μm. A similar morphology was observed by Mohamed et al. [24]. The chemical composition of the products was determined using EDS at various locations on the whiskers. From EDS results it was found that the mass fraction of Al and Si were 74.2% and 25.8%, which was in agreement with the stoichiometric composition of the mullite. In Fig. 4, the XRD analysis results further



AQ1 Fig. 3. The SEM photos of produced sample sintered at 1350°C for 2 h: (a) section of the membrane, (b) the top surface of the membrane, (c) transition layer between the top layer and the porous support, (d) support layer section..

confirmed that the generated whiskers were composed of mullite. There was a transition layer between the top layer and the porous support in Fig. 3c, which appeared to contain whiskers and flaky particles. Fig. 3d shows the microstructure of support layer section and it can be seen that the porous support had high porosity, and the pores were mutually connected with an excellent structure.

3.2. Phase analysis of the samples

The XRD patterns of the top-layer membrane of Sample AB and the support of Sample B sintered at 1350°C for 2 h are shown in Fig. 4. From Fig. 4 AB it appears that show complete orthorhombic mullite diffraction peaks because of the formation of mullite during the sintering. For the samples B, however, it appears that most strong diffraction peaks can be attributed to mullite. Additional, weak diffraction peaks appeared to result from the presence of cristobalite, which indicated besides mullite a small amount of cristobalite co-existed in the support. In summing up, the excess SiO_2 in kaolin can be consumed by adding alumina precursors and increase the amount of mullite, which is beneficial to obtain porous mullite membrane materials.

3.3. Pore parameters of sintered samples

3.3.1. Porosity

Fig. 5 shows the relationship between the porosity of the samples and the sintering temperature. From the results shown in this figure, it can be seen that the porosity of the samples decreased with the increase of sintering temperature, decreasing from 60.1% at 1250°C to 47.6% at 1400°C. This was related to the increasing sintering degree of samples with increasing sintering temperature. In addition, it can be seen that the porosity of the samples was more than 47% when they were sintered in the range between 1250°C and 1400°C. This may have resulted from the fact that the content of Al_2O_3 in the kaolin was less than 46 wt% and the rest of the porosity in this sample resulted mainly from the decomposition of the additive $Al(OH)_3$. The in-situ decomposition of $Al(OH)_3$ produced 60% of the volume contraction [25] which resulted in empty space in the matrix around the Al_2O_3 particles. During this process, the excess SiO_2 in the kaolin was rapidly consumed by the added alumina precursors accompanied by the formation of secondary mullite. When the free glassy phase was consumed, a stiff skeleton of a needle-like mullite structure was formed in situ, which provided high porosity. This high porosity was a necessary condition to ensure a negligible flow resistance of the membrane during filtration.

3.3.2. The pore size distribution and average pore sizes

The pore size distribution in the samples is shown in Fig. 6. As can be seen, the distribution in pore size in the porous mullite support is quite wide, ranging from 0.81

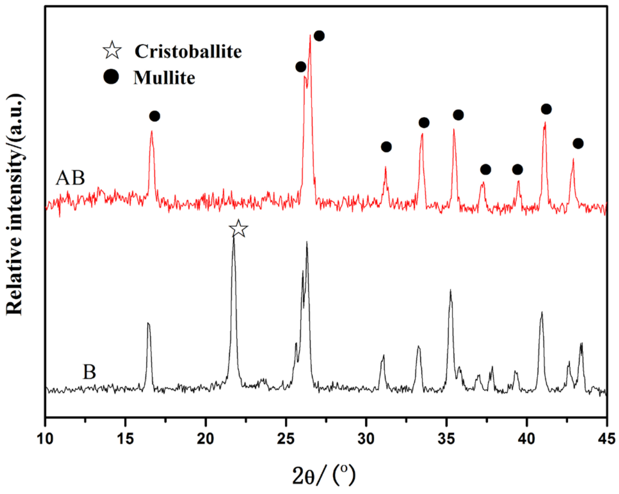


Fig. 4. XRD patterns of the top-layer membrane of Sample AB and the support of Sample B sintered at 1350°C for 2 h.

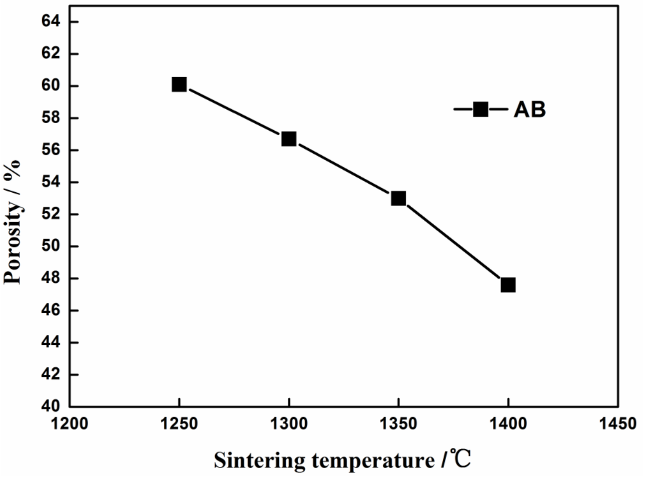


Fig. 5. Porosity of samples sintered at various temperatures for 2 h.

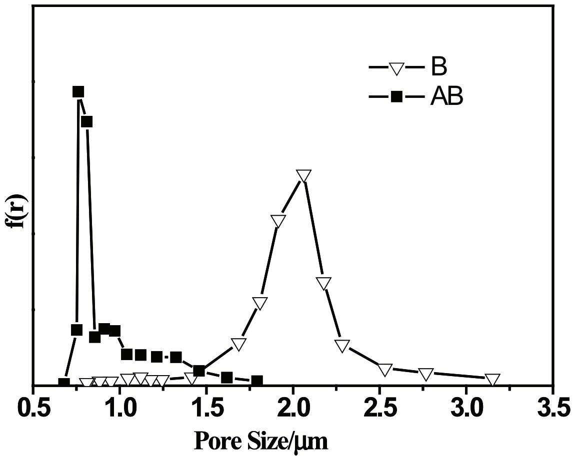


Fig. 6. Pore size distributions of the porous composite ceramic sintered at 1350°C: (B) porous mullite support, (AB) membrane after coating of mullite whisker.

to 3.2 µm. The most frequent pore size was 2.1 µm and the average pore size was 2.4 µm. The mullite whisker/mullite matrix composite samples exhibited significant shrinkage in pore size distribution with the pores ranging from 0.67 to 1.79 µm, with the most frequent pore size of 0.76 µm and an average pore size of 0.89 µm. A structure containing some mullite whisker with an acicular structure was prepared by coating a layer of precursor of mullite crystal whisker onto a porous mullite substrate, which was then fired with the base material. In the sintering process whiskers crossed each other to form a mesh structure so that the overall pore size distribution narrowed and the pore diameter decreased which improved the selection performance of the composite membrane material.

3.4. Permeability of sintered samples

The relationship between pure water volume flow and the operating pressure of Sample AB and Sample B is shown in Fig. 7. From the results shown in this figure, it can be seen that the pure water volume flow and operating pressure for each sample exhibited a linear relationship, which conformed well to Darcy's law [26]. It also can be seen that Sample B sintered at 1350°C exhibited a higher water flow volume than sample AB when tested using the same operating pressure. At 0.1 MPa operating pressure, the pure water flux of Sample B was 12728 $L{\cdot}m^{-2}{\cdot}h^{-1}$. After coating Sample AB with the mullite crystal whisker, at the same operating pressure, the pure water flow of Sample AB was 8776 $L{\cdot}m^{-2}{\cdot}h^{-1}$, indicating that the water flux was reduced by 31%. These results are shown to be caused by the dependence of the flow characteristic on pore size and porosity [27]. This was associated with the shrinking of internal pore structure of the sample, but the material still exhibited a very high water flux associated with its pore structure. The water flux of the membrane increased from 1.2 to 2 times compared to the existing microporous membranes of the similar pore size [10,28], which verified the basic hypothesis of this study.

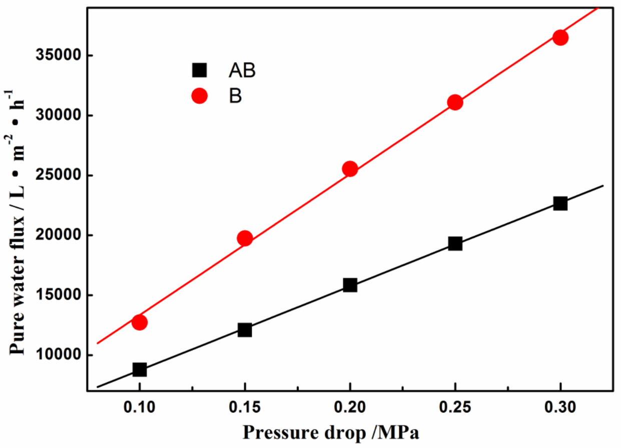


Fig. 7. Relationship between trans-membrane pressure and the pure water flux of samples: AB, B sintered at 1350°C for 2 h.

4. Conclusions

This results of this research effort showed that it is possible to directly obtain a high permeability porous mullite membrane material by designing a mesh structure that was formed from needle-like mullite. This membrane structure was formed by the addition of suitable alumina precursors as the top separation membrane materials and porous mullite in-situ to form the support structure. In the co-sintered preparation of the membrane free SiO_2 in the kaolin was consumed by the adding alumina precursors, so that a mesh structure was formed in-situ, which imparted suitable permeability to the final membrane. The co-sintering process simplifies the preparation of bilayer membranes, which could decrease the cost and production time thereby improving the possibility of industrial-scale production of the membrane. The bilayer membrane developed in this study can be used as a microfiltration membrane, particularly in high-throughput water treatment applications. This preliminary investigation was focused on the preparation of the membrane materials and future work is needed to examine the influence of membrane layer thickness during co-sintering and co-sintering of membrane layers with different pore sizes.

Acknowledgements

This work was supported by the central water resources fee into the special funds (126302001000150005), Natural science research project of Anhui Province (KJ2015B08), Scientific research fund project of Chuzhou University (2015qd13), Green chemical industry and core technology innovation platform of Chuzhou University, the Program in the Youth Elite Support Plan in Universities of Anhui Province (Grant No.gxyq 2017088).

References

[1] K. Suresh, G. Pugazhenthi, Development of ceramic membranes from low cost clays for the separation of oil-water emulsion, Desal. Water Treat., 57 (2016) 1927–1939.

[2] X.Z. Zhang, S.F. Suo, Y.H. Jiang, X.Q. Liu, Microstructure evolution and properties of YSZ hollow fibre microfiltration membranes prepared at different suspension solid content for water treatment, Desal. Water Treat., 57 (2016) 21273–21285.

[3] B. Das, B. Chakrabarty, P. Barkakati, Preparation and characterization of novel ceramic membranes for micro-filtration applications, Ceramics Int., 42 (2016) 14326–14333.

[4] B. Fan, G. Wei, H. Hao, A. Guo, J. Li, Preparation of a ceramic membrane from prevalent natural clay for the purification of phosphate wastewater, Desal. Water Treat., 57 (2016) 17308–17321.

[5] S.S. Kaplan-Bekaroglu, S. Gode, Investigation of ceramic membranes performance for tannery wastewater treatment, Desal. Water Treat., 57 (2016) 17300–17307.

[6] S. Sarkar, S. Bandyopadhyay, A. Larbot, S. Bandyopadhyay, New clay–aluminaporous capillary supports for filtration application , J. Membr. Sci., 392 (2012) 130–136.

[7] Q.B. Chang, J. Zhou, Y.Q. Wang, J. Liang, X.Z. Zhang, S. Cerneaux, X. Wang, Z.W. Zhu, Y.C. Dong, Application of ceramic microfiltration membrane modified by nano-TiO_2 coating in separation of a stable oil-in-water emulsion, J. Membr. Sci., 456 (2014) 128–133.

[8] L.L. Li, M.L. Chen, Y.C. Dong, X.F. Dong, S. Cerneaux, S. Hampshire, J.J. Cao, L. Zhua, Z.W. Zhua, J. Liu, A low-cost alumina-mullite composite hollow fiber ceramic membranefabricated via phase-inversion and sintering method, J. Eur. Ceram. Soc., 36 (2016) 2057–2066.

[9] L.L. Gong, Y.H. Wang, X.D. Cheng, R.F. Zhang, H.P. Zhang, Porous mullite ceramics with low thermal conductivity prepared by foaming and starch consolidation, J. Porous Mater., 21 (2014) 15–21.

[10] G.L. Chen, X.T. Ge, Y.Z. Guo, Y. Wang, W.H. Xing, Design and preparation of high permeability porous mullite support for membranes by in-situ reaction, Ceramics Int., 41 (2015) 8282–8287.

[11] Z.W. Zhu, Z.L. Wei, W.P. Sun, J. Hou, B.H. He, Y.C. Dong, Cost-effective utilization of mineral-based raw materials for preparation of porous mullite ceramic membranes via in-situ reaction method, Appl. Clay Sci., 120 (2016) 135–141.

[12] A. Pak, T. Mohammadi, Dehydration of water/1-1-dimethylhydraz-ine mixtures by zeolite membranes, Micropor. Mesopor. Mater., 70 (2004) 127–134.

[13] H. Katsuki, S. Furuta, A. Shiraishi, S. Komameni, Porous mullite honeycomb by hydrothermal treatment of fired kaolin bodies in NaOH, J. Porous Mater., 2 (1996) 299–305.

[14] H. Katsuki, H. Takagi, O. Matsuda, Fabrication and properties of mullite ceramics with needle-like crystals, Ceram. Trans., 31 (1992) 137–146.

[15] H. Katsuki, S. Furuta, S. Komarneni, Conventional versus microwave-hydrothermal leaching of glass from sintered kaolinite to make porous mullite, J. Porous Mater., 3 (1996) 127–131.

[16] Y. Saito, S. Hayashi, A. Yasumori, Effect of calcining conditions of kaolinite on pore structures of mesoporous materials prepared by selective leaching of calcined kaolinite , J. Porous Mater., 3 (1996) 233–239.

[17] Z.P. Lai, G. Bonilla, I. Diaz, Microstructural optimization of a zeolite membrane for organic vapor separation, Science, 300 (2003) 456–460.

[18] A.S. Huang, Q.A. Liu, N.Y. Wang, X. Tong, B.X. Huang, M. Wang, J. Caro, Covalent synthesis of dense zeolite LTA membranes on various 3-chloropropyltrimethoxysilane functionalized supports, J. Membr. Sci., 437 (2013) 57–64.

[19] J. Shao, Z.Y. Zhan, J.G. Li, Z.B. Wang, K. Li, Y.S. Yan, zeolite NaA membrane supported on alumina hollow fibers: effect of support resistances on pervaporation performance, J. Membr. Sci., 451 (2014) 10–17.

[20] X.B. Ke, H.Y. Zhu, X.P. Gao, J. Liu, Z. Zheng, High-performance ceramic membranes with a separation layer of metal oxide nanofibers, Adv. Mater., 19 (2007) 785–790.

[21] X.B. Ke, Z.F. Zheng, H.W. Liu, H.Y. Zhu, X.P. Gao, L.X. Zhang, N.P. Xu, H. Wang, H.J. Zhao, J. Shi, K.R. Ratin, High-flux ceramic membranes with a nanomesh of metal oxide nanofibers, J. Phys. Chem. B,112 (2008) 5000–5006.

[22] X.B. Ke, R.F. Shao, H.Y. Zhu, X.P. Gao, Ceramic membranes for separation of proteins and DNA through in situ growth of alumina nanofibres, Chem. Commun., 10 (2009) 1264–1266.

[23] L. Zhu, Y.C. Dong, S. Hampshire, L. Winnubst, Waste-to-resource preparation of a porous ceramic membrane support featuring elongated mullite whiskers with enhanced porosity and permeance, J. Eur. Ceram. Soc., 35 (2015) 711–721.

[24] G. Mohamed, M.U. Ismail, A. Hiroshi, T. Akiba, Mullite whiskers from precursor gel powders, J. Am. Ceram. Soc., 73 (1990) 2736–2739.

[25] Z.Y. Deng, T. Fukasawa, M. Ando, Microstructure and mechanical properties of porous Alumina ceramics fabricated by the decomposition of Aluminum hydroxide, J. Am. Ceram. Soc., 84 (2001) 2638–2644.

[26] S.J. Lukasiewicz, J.S. Reed. Specific permeability of porous compacts as described by a capillary model, J. Am. Ceram. Soc., 72 (1988) 1008–1014.

[27] P. Colombo, In praise of pores, Science, 322 (2008) 381–383.

[28] W.B. Peng, H. Qi, W.X. Li, W.H. Xing, N.P. Xu, Experimental investigation of effects of ceramic membrane channels on flux and optimization with CFD, J. Cem. Indust. Eng. (China), 59 (2008) 602–606.