Journal of Membrane Science 504 (2016) 29–39

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Preparation of zirconia nanofiltration membranes through an aqueous sol–gel process modified by glycerol for the treatment of wastewater with high salinity

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ARTICLE INFO

Article history:
Received 1 August 2015
Received in revised form
9 December 2015
Accepted 30 December 2015
Available online 9 January 2016

Keywords:
Zirconia
Membrane
High salinity
Nanofiltration
Aqueous sol–gel process

ABSTRACT

ZrO_2 nanofiltration (NF) membranes are attracting increasing interest for the treatment of wastewater with high salinity owing to the material stability and processing efficiency. This work presents an approach to synthesize zirconyl oxalate aqueous sols through a straightforward sol–gel route by introducing glycerol to modify zirconium oxychloride for fabricating a pure tetragonal ZrO_2 NF membrane with high permeable and separation performance. The glycerol, acting as a capping agent, binds to the surface of the sol particles resulting in stable nano-sized sol particles and then inhibiting the t→m phase transformation when calcination at 400 °C. A crack-free ZrO_2 NF membrane with a molecular weight cut-off of 750 Da and a permeability of 13 $L\,m^{-2}\,h^{-1}\,bar^{-1}$ was prepared. By comparing to the reference system with polymeric NF membrane for the treatment of model wastewater with high salinity, we demonstrate that, both ZrO_2 and polymeric NF membranes show similar retention performance (higher than 90%) of pure polyethylene glycol (molecular weight = 1000). However, at the high NaCl mass fraction varying from 0% to 24.92%, the ZrO_2 NF membrane displays much better retention performance at about 68% while only 36% for polymeric NF membrane. Our results indicate the potential application of ZrO_2 NF membranes in the wastewater with high salinity.

1. Introduction

Many chemical industries (pharmaceuticals, agrochemicals, etc.) generate wastewater containing organic substances and inorganic salt during the respective production processes. An increasing focus on the protection of the environment and the quality of products makes the recovery of such waste products and/or the implementation of desalination more important today [1,2]. NF technology is potentially the best candidate to solve the problem because it can separate low-molecular-weight solutes from an inorganic salt solution [1,3]. Ceramic NF membranes are known for their chemical, thermal and mechanical stability. One of the distinctive characteristics of ceramic NF membranes is their ability to withstand strong doses of chlorine. These advantages make ceramic NF membranes more favorable than polymeric NF membranes for the treatment of wastewater with high salinity.

To date, ceramic NF membranes with different types of materials have been fabricated, including γ-Al_2O_3 [4,5], TiO_2 [6–8], ZrO_2 [9–12], SiO_2 [13–15], SiO_2–ZrO_2 [16,17] and TiO_2–ZrO_2 [18–20] NF membranes. Among them, the ZrO_2 membranes are more suitable for liquid-phase applications under harsh conditions due to their higher chemical stability compared to other ceramic materials. The sol–gel process is considered to be the main technique for the preparation of ZrO_2 NF membranes, and the polymeric sol–gel process is the most frequently utilized route, in which the precursor is partially hydrolyzed with a less than equivalent amount of H_2O and large amounts of organic solvents were added during the reaction course. By contrast, the colloidal sol–gel route is preferred due to its advantageous low volatilization and easy operation, offering the more possibility of the industrial-scale process. However, few works have been reported in the literature regarding the preparation of ZrO_2 NF membranes using the colloidal sol route [21]. The difficulty regarding the preparation of ZrO_2 NF membranes via the colloidal sol–gel technique is to preserve individual grains of less than 10 nm throughout the process, in view of the particle packing models of random closed-packed systems [22,23].

Indeed, two main challenges will be encountered throughout the colloidal sol–gel process. The first challenge is to synthesize

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http://dx.doi.org/10.1016/j.memsci.2015.12.068

sols with particle size smaller than 10 nm to yield nanophase ceramics with a narrow pore size distribution [22]. Coterillo et al. [21] produced stable ZrO_2 sols with a hydrodynamic diameter of 7.8 nm by adjusting the precursor concentrations in the range of 0.5–2 wt%; the microporous ZrO_2 membranes prepared by coating the sols have been used for gas permeation at 200 °C. It is to be noted that because of the extremely rapid reaction of zirconium alkoxide with water, organic solvents are often required to effectively control the reactivity during the reaction course [24]. Hence, the aqueous sol–gel process derived from inorganic salt might be a worthwhile and economical option due to the advantages of the inexpensive precursor and the environmentally friendly process [25,26]. For example, Etienne et al. [27] introduced the use of zirconyl salt in an aqueous sol–gel process and prepared a colloid sol with an average diameter of 14 nm. Ju et al. [28] produced aqueous sol particles with size larger than 100 nm via a similar process. Such behavior may occur because nano-sized sol particles with a high surface energy are formed via complete hydrolysis and because these particles favor aggregation of large particles [29]. Hence, producing a highly stable ZrO_2 sol with particle size below 10 nm could be a challenge of an aqueous sol–gel process.

Thermal treatment is another parameter that can affect the grain growth responsible for the pore structure increase. Moreover, the pure ZrO_2 membranes may form cracks because of the stresses developed associated with phase transformation from tetragonal to monoclinic phase during heating treatment. It is proposed that the presence of oxygen ion vacancies within nanocrystalline ZrO_2 particles is primarily responsible for room-temperature stabilization of the tetragonal phase below a critical size [30]. In addition, a suitable cation doping in the ZrO_2 lattice is known to stabilize tetragonal phases by creating oxygen vacancies to yield energetically favored structures [31–35], depending on the generation of oxygen ion vacancies and their association with the host Zr^{4+} cations. Dobrosz-Gomez et al. [32] produced Ce–Zr mixed oxides with a crystallite size of 6.7 nm that exhibited a specific surface area of 46.5 $cm^2\,g^{-1}$ at 550 °C. Vacassy et al. [35] synthesized ZrO_2/MgO with a crystallite size of 5.3 nm and a specific surface area of 177.2 $cm^2\,g^{-1}$ at 400 °C.

In fact, there exists one effective way to address the two challenges mentioned above. The excess oxygen ion vacancies that result from the combustion of residual carbonaceous material and the nanocrystal size effect could lead to stabilization of the metastable tetragonal phase structure, which differentiated the doping mechanism. Huang et al. [36] found that after introducing glacial acetic acid and DMF, the crystallite size of ZrO_2 decreased from approximately 26.48–13.94 nm when calcination was performed at 600 °C for 40 min. Furthermore, in our previous work, Cai et al. [37] compared two types of organic species that were introduced during the reaction course, and the results revealed that glycerol helps to synthesize TiO_2 hydrosol with a mean particle size of 5 nm and to restrain the phase transformation of TiO_2 material. A crack-free, pure TiO_2 NF membrane with a molecular weight cut-off (MWCO) of 800 Da was prepared via a colloidal sol–gel route derived from alkoxide, while the procedure involves the use of organic solvent due to the alkoxide precursor [37].

In this study, glycerol was introduced during the fabrication of a ZrO_2 NF membrane via an aqueous sol–gel process derived from inorganic salt. The effects of glycerol concentration on the ZrO_2 membrane material structure and particle morphology are discussed in detail, with a special emphasis on the mechanisms of the tetragonal phase stabilization in the ZrO_2 structure. Furthermore, to gain better insight into their separation behavior in the treatment of wastewater with high salinity, comparisons were made between polymeric NF membranes and ceramic NF membranes with a similar MWCO for the treatment of model wastewater. This study is useful in the development and application of ceramic NF membranes in the separation of species from an inorganic salt solution.

2. Experimental

2.1. Membrane preparation

2.1.1. Synthesis of sol

A stable 0.05 M zirconyl oxalate ($ZrOC_2O_4$) sol was prepared from an aqueous solution of zirconyl chloride octahydrate ($ZrOCl_2\cdot 8H_2O$, Sigma-Aldrich, 98%) and oxalic acid dihydrate ($H_2C_2O_4\cdot 2H_2O$, Sigma, ≥99.5%). $ZrOCl_2\cdot 8H_2O$ was dissolved in 150 mL of deionized water with the desired amounts of glycerol (Sigma-Aldrich, ≥99%). Meanwhile, $H_2C_2O_4\cdot 2H_2O$ was dissolved in 50 mL of deionized water as complexing agent. While the solution was stirred, an $H_2C_2O_4$ solution was added drop wise to the $ZrOCl_2$ solution at 60 °C, and then the solution with a $[ZrOCl_2]/[H_2C_2O_4]$ molar ratio of 5:1 was mixed. After 30 min, the temperature was gradually increased to 80 °C and maintained for 3 h to obtain the stable colloidal sol. Compositions containing glycerol in the total weight percentages of 0, 0.18, 0.35 and 0.5 were noted as ZZ, ZZ18, ZZ35 and ZZ50, respectively, which corresponds to the molar ratio of glycerol and $ZrOCl_2$ of 0:1, 0.4:1, 0.8:1 and 1.2:1.

2.1.2. Preparation of ZrO_2 NF membranes

The ZrO_2 NF membrane layer was coated onto an asymmetric tubular support, and the procedure was similar with the previously reported literature [37,38]. The support was prepared in the laboratory, had an inner diameter of 8 mm and a length of 110 mm, and contained an α-Al_2O_3 ultrafiltration layer by applying the colloidal sol–gel route. The formed UF-membranes (with a MWCO of 30 kDa) are used as supports for subsequent NF layer coating experiments. Polyvinyl alcohol (PVA, Sigma-Aldrich, molecular weight = 61,000 Da, 10 wt% aqueous solution) and glycerol were introduced into the $ZrOC_2O_4$ sols prior to coating to adjust the viscosity of the sol and to act as drying control chemical additives. The amount of polymer additives was approximately 7.5% PVA aqueous solution and 6% glycerol in 40 g of $ZrOC_2O_4$ sol. The sol was used to coat the inner surface of the support to develop the NF membrane.

After coating the sol onto the α-Al_2O_3 UF-membranes for 10 s, the wet membranes were transferred to an oven at 60 °C with a relative humidity of 60% for 12 h. Next, a gradual thermal treatment was applied [39], heating the membranes first for 12 h at 60 °C, then for 12 h at 100 °C, and, finally, for 12 h at 110 °C. The membranes were then sintered at 400 °C for 2 h in a muffle furnace (at a heating and cooling rate of 0.25 and 0.5 °C min^{-1}, respectively). All of the procedures were performed once to obtain tubular ZrO_2 NF membranes. Non-supported gel layers were produced by pouring the excess sol into Petri dishes, and the subsequent dry-calcination procedure was the same as that for the supported membranes. To investigate the crystal growth behavior of nanocrystalline ZrO_2 after calcination, the ZrO_2 samples were further heat treatment at different temperatures, i.e., 500 °C, 600 °C, 700 °C, 800 °C and 900 °C.

2.2. Characterization

2.2.1. Structural characterization

The viscosity of the $ZrOC_2O_4$ sol was determined using a rotary viscometer (DV-II+, Brookfield, USA) at 30 °C. The particle size distribution of $ZrOC_2O_4$ sol was measured using the dynamic light scattering technique (ZetaPALS, Brookhaven, USA). For the XRD, HRTEM and N_2 adsorption–desorption isotherm analyses, the ZrO_2 materials were ground into fine powders. The crystalline phases of