



Fabrication of novel hierarchical ZSM-5 zeolite membranes with tunable mesopores for ultrafiltration

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ABSTRACT

A series of novel hierarchical ZSM-5 zeolite membranes with tunable mesopore sizes have been prepared successfully by using amphiphilic organosilane 3-[(trimethoxysilyl) propyl]octyldimethyl-ammonium chloride (TPOAC) as the mesogenous template and part of the Si source. The effects of several synthesis parameters, such as the TPOAC/SiO₂ ratio, synthesis temperature and crystallization time, on the microstructures and rejection performance of the hierarchical ZSM-5 zeolite membranes were systematically investigated. Multiple techniques, such as XRD, SEM, N₂ adsorption techniques, TEM, IR, ¹³C MAS NMR and ²⁹Si MAS NMR were employed for the characterizations. The filtration of dextran in water shows that the membranes have molecular weight cutoff (MWCO) ranging from 9500 to 943,000, corresponding to the molecular size in the range of 4.5–37 nm. The sharp increase in the rejection of dextran with the increase of molecular weight indicated narrow pore size distribution of the membrane. These results show that the hierarchical mesoporous ZSM-5 zeolite membranes have a great potential for ultrafiltration with high performance.

1. Introduction

Ultrafiltration is a pressure-driven, membrane-based separation process, which is used for a broad variety of applications, ranging from the processing of biological macromolecules to wastewater treatment. Ultrafiltration membranes are defined as having a pore size in the range 2–100 nm and generally classified into two major groups according to their materials properties: polymeric membranes and ceramic membranes. At present, polymeric membranes hold dominant position in filtration progress due to their simple preparation and affordable price. However, some shortcomings like biofouling, low mechanical strength, poor solvent resistance hinder their application. Ceramic membranes with the properties of high mechanical strength and good chemical stability have received much attention [1].

Ceramic ultrafiltration membranes are mostly prepared by sol-gel method. In this method, the original sols, formed by hydrolysis and condensation of metallorganic precursors, are firstly coated on the suitable support, followed by calcination to fabricate a thin film of closely packing [2]. The average pore sizes of membranes derived from particle packing are mainly determined by particle size distribution. However, the sol nanoparticles grow larger easily because of the rapid hydrolysis and condensation of precursors, which makes it quite difficult to control the pore size of the membrane obtained consequently [3–5]. Meanwhile, high sintering temperature, usually above 1000 °C,

leads to high energy consumption. Therefore, it is significant to develop a new kind of inorganic ultrafiltration membranes which can be prepared in a simple, reproductive and low cost method.

Zeolite membrane, a kind of important inorganic membrane material with well-defined pore size as well as the thermal, chemical, and mechanical stability of ceramics, have been studied extensively for many potential applications, especially as separation [6]. Their pore sizes, typically in the range of 0.3–1 nm, make them highly suitable for various molecular level separations including gas phase [7] and liquid phase mixtures [8,9]. In general, permeation in an ideal molecular sieve zeolite membrane should occur only through the regular intracrystalline pores of the zeolite selective layer. In reality, however, most zeolite membranes reported so far contain inter-crystalline defects, which caused by insufficient inter-growth of crystals [10], thermal removal of the template [11,12], or dehydration of the membrane layer [13]. These defects, especially those larger than the zeolite pores, has led to a different membrane performance, underestimation of selectivity, and overestimation of permeance. Therefore, various post-treatment methods to eliminate or reduce these defects have been investigated in order to improve separation selectivity [14,15].

On the other hand, it is well accepted that, even the grain boundary defects are not desirable, they inevitably form between the grains during hydrothermal growth since zeolite membranes grow by competitive growth [6]. If the size of such boundary defect porosity could

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be controlled within the range of 2–100 nm, then this new kind of hierarchical zeolite membrane, containing both micropore and mesopore systems could be obtained, and used as novel ultrafiltration membrane.

Until now, considerable efforts have been made to introduce mesopores into zeolite and the obtained hierarchical zeolites have been extensively applied in the field of catalysis [16]. Hierarchical zeolites mostly made by post-synthetic modification or templating approaches provide higher specific surface area and larger pore size that improve the mass transfer rate. The post-synthetic modification, such as dealumination [17] and desilication [18] have proven to be efficient in creating mesopores in zeolite crystals. However, it is hard to create uniform mesopores with these methods. Furthermore, loss of relative crystallinity and the partial dissolution of the parent zeolite cannot be avoided during these processes [19]. Compared with post-synthetic modification, template directing method, especially soft-templates method is another popular method to synthesis of hierarchical zeolites because of its convenient operation. Various mesogeneous templates, such as cationic surfactant (CTAB) [20], cationic polymer [21], silylated polymer [22], and nonionic alkyl poly(ethylene oxide) surfactants [23] have been used to create mesopores in the zeolite with the present of a structure-directing agent for the synthesis of zeolite. However, under most circumstances, the two different templating systems, microporous template and the mesopore structure-directing agent, work in a competitive rather than a cooperative manner, which may result in the formation of a physical mixture containing amorphous mesoporous material and bulk zeolite without mesoporosity [19]. To address this issue, Ryoo et al. successfully prepared a range of amphiphilic organosilanes, which can simultaneously provide part of the silica source and act as mesopore-directing agent that avoid phase separation [24–26]. Typical example is amphiphilic organosilane 3-[(trimethoxysilyl) propyl]octyldimethyl-ammonium chloride (TPOAC) and its structural analogues. The synthesized zeolites possessed high mesopores and the mesopore diameters could be tuned according to the tail length of organosilane, synthesis temperature and crystallization time [24].

Al-substituted MFI zeolite membrane, also called ZSM-5 zeolite membrane, possesses uniform pore size of 0.55 nm and adjustable ratio of Si/Al with the potential to achieve large permeation and selectivity for separation of aqueous solutions [27]. In this paper, we present the one-pot synthesis of hierarchical ZSM-5 zeolite membranes with TPOAC on four-channel ceramic hollow fibers. The as-synthesized membranes with tunable boundary defect pore size, exhibited a good separation performance at a low pressure for nanometer-sized separation. Moreover, our method has certain advantage for the fabrication cost of selective top layer. Because using zeolite membrane as separation layer, its synthesis is through a one-step hydrothermal treatment, and the temperature to remove template from the zeolite is lower. For the ultrafiltration ceramic membrane with small pore size, the preparation usually needs repeated coating and sintering at high temperature. So the simple preparation as well as the low calcination temperature can significantly reduce the production cost, which makes this new ZSM-5 zeolite membrane a promising ultrafiltration material.

2. Experimental

2.1. Materials

The four-channel porous Al_2O_3 hollow fiber with high mechanical strength and low transfer resistance used as substrates were fabricated by a dry-wet spinning technique. They offered an outer diameter of 3.8 mm, an average pore size of $\sim 0.55 \mu\text{m}$ and a high porosity of $> 50\%$. The detailed preparation procedure was reported in our previous publication [28]. All chemical reagents used, i.e. tetrapropylammonium hydroxide solution (TPAOH, 1.0 M in H_2O), sodium hydroxide (NaOH, 99.99 wt%), aluminium sulfate octadecahydrate

($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, $> 98 \text{ wt}\%$), fumed silica (SiO_2 , powder $0.007 \mu\text{m}$) were purchased from Sigma Aldrich while amphiphilic organosilane 3-[(trimethoxysilyl) propyl]octyldimethyl-ammonium chloride (TPOAC) was purchased from Aladdin. All chemical reagents were of analytical grade and used as received without further purification.

2.2. Synthesis of silicalite nanoparticles

The silicalite-1 nanoparticle seeds were synthesized by a hydrothermal methodology according to a work previously reported [14]. In a typical synthesis procedure, 8 g of fumed silica and 0.56 g of NaOH pellets were dissolved into 40 mL of 1 M TPAOH solution to obtain a mixture with agitation at $80 \text{ }^\circ\text{C}$. Then, the precursor was aged at room temperature for 3 h. The resulting mixture was transferred into a teflon lined stainless steel autoclave for hydrothermal treatment at $60 \text{ }^\circ\text{C}$ for 14 d. Then the precipitate was recovered by centrifuge and washed with distilled water and dried in oven overnight. Coating suspensions were prepared by dispersing 0.2 g silicalite particles into 20 mL of aqueous solution comprising 0.1 wt% hydroxypropyl cellulose (HPC). The macromolecular additives of HPC were used to improve binding between the seeds and the substrate surface after calcination. Seeding suspension was stirred until dip-coating.

2.3. Preparation of hierarchical ZSM-5 zeolite membrane

The hierarchical ZSM-5 zeolite membranes were synthesized on four-channel porous Al_2O_3 hollow fibers by the secondary growth method. Firstly, the hollow fiber was immersed vertically in seeding suspensions for 20 s. The seeded hollow fibers were dried in an oven at $60 \text{ }^\circ\text{C}$ overnight and then calcined at $450 \text{ }^\circ\text{C}$ for 6 h.

To prepare synthesis solution, a certain amount of TPOAC was firstly added into deionized water and stirred until completely dissolved, then NaOH, and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ were added consequently. Finally, fumed silica was dissolved in the mixed solution at $80 \text{ }^\circ\text{C}$ under magnetic stirring. After further stirring for 3 h at room temperature, the synthesis solution with a molar composition of $160 \text{ SiO}_2 : 1.0 \text{ Al}_2\text{O}_3 : 46 \text{ Na}_2\text{O} : (0\text{--}6.4) \text{ TPOAC} : 22168 \text{ H}_2\text{O}$ was poured into the teflon lined stainless steel. The seeded hollow fibers were subsequently immersed into the synthesis solution vertically and heated at a temperature range of $170\text{--}200 \text{ }^\circ\text{C}$ for 15–60 h under tumbling conditions at 2 rpm. After hydrothermal crystallization, the as-synthesized membranes were washed thoroughly with deionized water, dried in an oven overnight and calcined at $550 \text{ }^\circ\text{C}$ for 6 h to remove template.

2.4. Characterizations

The volume particle size distribution and the average particle size of silicalite-1 nanoparticle seeds were characterized by a laser scattering particle analyzer (Zetasizer, Nano-ZS90, Malvern, UK). An X-ray diffraction (XRD, Rigaku MiniFlex 600) with a Cu-K α radiation source in the 2θ range of $5\text{--}50^\circ$ at a scan rate of $10^\circ \text{ min}^{-1}$ was used to measure the crystal phases. The surface morphology and cross-sections of zeolite membranes were observed by scanning electron microscopy (SEM, Hitachi S-4800) operated at 5 kV and $10 \mu\text{A}$. Fourier transformed infrared spectrometer (FTIR, Nicolet, USA) by using KBr pellets technology in the range of $400\text{--}4000 \text{ cm}^{-1}$ was employed to detect the incorporation of amphiphilic organosilane into the ZSM-5 structure. Transmission Electron Microscope (Tecnai G2 F30 S-Twin, FEI, USA) at an accelerating voltage of 200 kV was applied to observe the microscopic morphologies. The N_2 adsorption-desorption isotherms at 77 K were measured by Micromeritics surface area analyzer (ASAP 2020, Micromeritics, USA), the surface area values and average pore diameters were obtained by application of the BET equation. ^{13}C magic-angle-spinning (MAS) nuclear magnetic resonance (NMR) and ^{29}Si cross-polarization (CP)/MAS NMR analyses were carried out on a Bruker AvanceIII 400 spectrometer.

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