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Synthesis of ZSM-5 zeolite membranes without organic templates using a varying-concentration technique

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Abstract: Template-free nanosized ZSM-5 seeds with an average size of 15 nm were prepared from a synthesis solution with the composition $12Na_2O:100SiO_2:2Al_2O_3:2500H_2O$. By the use of these seeds, thin ZSM-5 zeolite membranes were prepared on the outer surface of a porous α-alumina tube with a pore size of 2 μm in a gel system by varying-concentration synthesis with organic-free template. The first composition synthesis sol-gel was the same as seeds of molar composition and the second one was $12Na_2O:100SiO_2:2Al_2O_3:5000H_2O$ at 180 ℃ for 10 h, respectively. XRD shows that the film consists of well-crystallized ZSM-5 zeolite. SEM investigation indicats that the zeolite films on the supports are defect free and the film thickness is approximately 8 μm. The permeances for H_2, N_2, CH_4 and CO_2 are 8.94×10^{-7}, 3.27×10^{-7}, 3.9×10^{-7}, 3.14×10^{-7} and 0.874×10^{-7} $mol\cdot m^2\cdot s^{-1}\cdot Pa^{-1}$, respectively. The ideal selectivity of membrane at room temperature for H_2/CO_2, H_2/N_2, H_2/CH_4 are 2.84, 2.73 and 2.29, respectively.

Key words: template-free; varying-concentration synthesis; ZSM-5 zeolite membrane; permeance; ideal selectivity

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1. Introduction

Zeolite membranes have advantages of unique pore structures and adsorption properties, superior thermal, mechanical and chemical properties, so they can be used in the separation of liquid and gas. ZSM-5 zeolites have MFI structure, their developed duct system offers possibility for molecule proliferation and not easy to block up, thus they have a prospect of wide application in high temperature separation. Therefore they will have extensive solicitude from membrane researchers[1-5].

ZSM-5 zeolite membranes are generally synthesized in the presence of organic templates agent, usually the tetrapropylammonium cation. While ZSM-5 zeolite membranes are showing high performance after calcination at high temperatures exceeding 400 ℃, several studies have shown that microcracks tend to form in thin zeolite membranes during calcination due to the thermal stress, which was caused by the difference in thermal expansion between zeolite layer and support and by changes in lattice parameters of zeolite crystals as a consequence of the removal of templates agent. One way to avoid the calcination step is to synthesize ZSM-5 zeolite membranes without the use of organic templating agent. Such attempts have recently been reported[6-10].

2. Experimental

2.1. Synthesis of ZSM-5 zeolite seeds

A template-free ZSM-5 seed with an aver-

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age size of 15 nm prepared from a synthesis solution was prepared by 4.0 g dissolving sodium hydroxide(NaOH ≥ 96.0 wt.%, A.R, Shanghai Chemical Reagent Co.Ltd.) and 1.64 g sodium aluminates ($NaAlO_2$ L. R, Shanghai Chemical Reagent Co.) in 135 g deionized water in beaker. The contents of the beakers were carefully mixed and a 104.3 ml silica sol (25 wt.%, Shanghai Second Reagent factory) was slowly added to the above solution under continuous stirring. The molar composition of the resulting synthesis gel was $12Na_2O : 100SiO_2 : 2Al_2O_3 : 2500H_2O$. Prior to being transferred to a Teflon-lined stainless steel autoclave, the above synthesis solution was aged for 12 h at room temperature and then was hydrothermally treated for 24 h on an oven at a temperature of 180 ℃. After the hydrothermal treatment, the seeds were recovered, thoroughly washed with deionized water, and then dried at 100 ℃.

2.2. Preparation of membranes

A porous α-Al_2O_3 tube (Nanjing Industry University, China, 13 mm o.d. and 8 mm i.d., 40 mm length) with an average pore size of 2 μm, and porosity of 38% - 40%, was used as the support for zeolite membrane. The surface of the support was polished with sand paper on both sides, after which the support was immersed for 24 h in 10 $mol \cdot L^{-1}$ hydrochloric acid and sodium hydroxide priority and cleaned with demonized water in ultrasonic cleaner for 10 min. The process was repeated three times to remove the loose particles created during polishing. The cleaned support was dried at 120 ℃ and calcined at 550 ℃ for 3 h, with heating and cooling temperature of 1 $℃ \cdot min^{-1}$.

A template-free ZSM-5 seed with an average size of 15 nm weighing 1.0 g was first ground in a porcelain mortar. The ground powder was then mixed with an appropriate amount of deionized water in a beaker to form slurry. The slurry was treated in an ultrasonic bath for 30 min at room temperature. The concentration of the crystals in the suspension can be adjusted by the addition of deionized water. In this study, a colloidal suspension with the solids content of 0.5% and pH = 8 was used for seeding. The seeding was carried out as follows. The support was dipped in the colloidal suspension for 2 min, withdrawn vertically at a slow rate of approximately 0.5 $cm \cdot s^{-1}$, and then dried for 30 min at 20 ℃ and subsequently for 30 min at 120 ℃. This process was run twice.

The synthesis gel was prepared by 2.48 g dissolving sodium hydroxide and 0.492 g sodium aluminates in 112 g deionized water in beakers. The contents of the beakers were carefully mixed and 41.85 ml silica sol was slowly added to the above solution under stirring. The first and second molar compositions of the resulting synthesis gel were $12Na_2O : 100SiO_2 : 2Al_2O_3 : 2500H_2O$ and $12Na_2O : 100\ SiO_2 : 2Al_2O_3 : 5000\ H_2O$, respectively. Each end of the tube was wrapped with Teflon rod and placed vertically in the autoclave with Teflon-lined, about 30 ml aged zeolite synthetic solution was carefully poured into the autoclave along the supports. The first and second hydrothermal treat were sealed and placed in an oven preheated to 453 K for 10 h, respectively. After the hydrothermal synthesis, the composite membranes were cooled and washed thoroughly with deionized water until the pH value of the washings was neutral, then dried at room temperature for 12 h, and dried at 373 K for 12 h.

2.3. ZSM-5 zeolite seeds and membrane characterization

The synthesis seeds and crystallographic properties of the α-Al_2O_3 supported ZSM-5 membranes were examined with X-ray diffraction (XRD, D8-Advance German Bruker Co.) using λ = 0.15046, Cu Kα radiation. Room temperature infrared transmission spectra were investigated to define the degree of crystallization using a fourier transform infrared (FTIR) spectrometer (MB154S, Canada Bomem Co.). FTIR measurements were performed only in the mid-infrared range of instrument (400 - 4000 cm^{-1}) for samples dispersed in KBr pellets in 1:99 ratio. The particle size and the nature of its external surface of synthesis seeds were determined by transmission electron microscopy