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Permeation properties of templated and template-free ZSM-5 membranes

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Abstract

Following the secondary growth procedure, ZSM-5 zeolite membranes were synthesized over porous alpha-alumina supports from clear template-free precursor solution and their permeation properties were compared with membranes prepared using templates. SEM analysis revealed that the templated membrane (M1) contained smaller crystals with more number of faces than their template-free counterpart (M2). Identical XRD patterns confirmed their ZSM-5 crystal structure. The expected size selectivity could not be achieved for M1 as this membrane possessed some micro defects, induced by the calcination procedure. M2 could achieve the required size selectivity at ambient temperatures and shape selectivity at 200 °C and gas permeation was mostly activated diffusion. Selectivity ratio of 44 was achieved for butane isomers through M2 with *n*-butane molecules experiencing maximum activation (43 kJ/mol). In general, permeation values measured for M2 membranes were an order lower than those of M1 membranes.

Keywords: Zeolite membrane; ZSM-5; Template-free; Permeation; Comparison

1. Introduction

Zeolite membranes find immense applications such as in catalytic membrane reactors, as sensors, and for gas/liquid separations. Many reviews deal with the synthesis and properties of zeolite membranes and their applications [1–3]. Ideally, the formation of a good zeolite membrane requires a thin, continuous, defect-free and nearly two-dimensional layer of zeolite crystals so that the transport across the membrane takes place only through the zeolite pores. Even though various zeolite species were investigated for membrane applications, the majority of the work concentrates on MFI type zeolite ZSM-5 and its aluminum-free analogue, silicalite, because of its pore structure, similar to many industrially important molecules, thereby contributing its potential as a separation device.

Usually, zeolite membranes were synthesized by direct hydrothermal treatment using organic structure-directing molecules (mostly tetrapropylammonium ions, TPA^+), which gets incorporated inside the pore structure. These templating molecules have to be removed by calcination in order to expose the zeolite pores. But this process induces cracks in the membrane structure, which makes it less effective for its intended application. It is also possible to avoid organic templates from the synthesis solution and still ensuring crystal formation [4].

The introduction of a secondary (or seeded) growth method brought in improved flexibility for crystal growth and greater control of film microstructure as well as greater reproducibility and scalability [5]. In this process, a thin and uniform layer of seed crystals deposited on the substrate surface were further allowed to grow under hydrothermal conditions in the presence of template molecules to produce a membrane layer. Couple of recent works depicts the procedure to make such membranes without using organic templates as well [6,7]. As reported in the literature, the membrane processing by the templated and template-free methods follow significantly different procedures and demands separate attention. This paper compares the variation in properties of ZSM-5 membranes synthesized by these two methods; for easiness of comparison, methods and materials were kept identical whenever this is practically possible.

2. Experimental

2.1. Membrane preparation

Alpha-alumina substrates of pore size 1.2 μm (Noritake Co. Ltd., Japan) were used as substrates. Both ends of the

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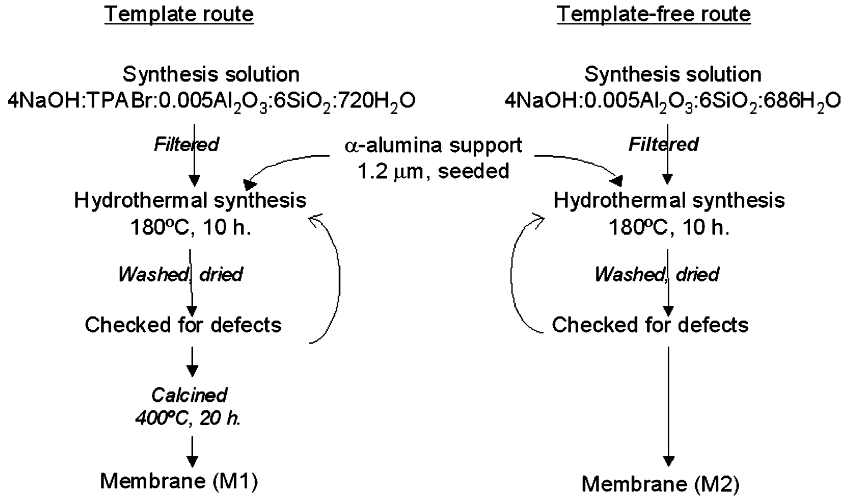

Fig. 1. Flow chart depicting the synthesis procedures used to prepare M1 and M2.

substrates were glazed to expose 2 cm in the middle portion, which was seeded as follows: The Na-ZSM-5 seeds were thoroughly dispersed in water, adjusting the pH to 8 and a pre-cleaned substrate was immersed into this seed solution. The seed solution was slowly drawn out using a peristaltic pump so that the seed attaches to the support by electrostatic attraction and surface adhesion. The dip-coated substrate was dried at ambient conditions and were secondary grown to form zeolite membranes by hydrothermal synthesis using a clear precursor solution of molar composition (A) $4NaOH:TPABr:0.005Al_2O_3:6SiO_2:720H_2O$, using TPABr template (M1)and (B) $4NaOH:0.005Al_2O_3:6SiO_2:686H_2O$, without using template (M2). The mother liquor was prepared by dissolving NaOH and $Al(OH)_3$ (and TPABr for composition A) in water and mixing it with fumed silica solution under vigorous stirring at 80 °C, until a visibly clear solution was obtained. It is then filtered using a teflon filter paper (Millipore; 0.1 µm) to derive a uniform clear solution, which is transferred to a teflon-lined stainless steel autoclave and seeded substrates were introduced vertically. The autoclave is then heated in an air-oven at 180 °C for 10 h. After the synthesis, the autoclave is cooled down to room temperature and the substrate was washed thoroughly with water, dried at 50 °C and tested for defects using SF_6 permeation measurements. Membrane prepared using template (M1) was calcined at 400 °C (heating rate of 0.5 °C/min) for 20 h to remove the templates occluded in the zeolite pores during synthesis. A flow-chart describing the synthesis procedure is given in Fig. 1.

Membranes were characterized by X-ray diffraction (XRD; Rigaku RINT2400) and surface morphology was observed using field emission-scanning electron microscope (FE-SEM; Hitachi S-900S). Complete removal of organic matter from the zeolite pores was confirmed using thermogravimetic measurements (TG; Perkin-Elmer TGA7). Membrane portion was carefully scrapped off from the alumina support for TG and surface area measurements (Micromeritics, ASAP 2010). Elemental composition was measured using energy-dispersive X-ray analysis (EDX; Hitachi S-3200N) method.

2.2. Permeation measurements

Single gas permeation measurements were made using dead-end method for H_2, He, CO_2, N_2, CH_4, n-C_4H_{10}, i-C_4H_{10} and SF_6 molecules. Pre-seeded tubular substrates were fixed inside the stainless steel permeation cell using Viton O-rings. One end of the permeation cell was sealed (dead-end) and dried single component gases were fed through the outer side while the downstream was evacuated. Prior to the measurements, both sides of the membranes were evacuated at 200 °C for about 20 h. At the measurement temperature, the permeation cell was allowed to stabilize for 2 h under He flushing and the measurements were made at 200, 150, 75 and 30 °C. For permeation measurements, the vacuum line is closed and the increase in pressure inside the reservoir is monitored with respect to time. To eliminate contamination, the membrane was thoroughly flushed with He between successive measurements, until the initial He permeance values were achieved.

3. Results and discussion

3.1. Characterization

The primary aim of this study was to compare the permeation properties between ZSM-5 membranes synthesized by two different routes. Both these membranes were synthesized using secondary growth protocol (seeded growth) and their composition was kept identical for comparison except for higher dilution when template molecules were involved. In fact, the zeolite film growth is known to involve complex processes in which both substrate and reaction mixture has equal contribution. Here, since the substrate properties were kept constant, the difference is brought in by the synthesis gel in which the presence and absence of template molecules poses an important variable. Other important synthesis parameters like temperature, aging of synthesis mixture, composition effects like alkalinity, ionic strength, etc., also influence crystal growth during membrane formation and hence need to be dealt separately. FE-SEM reveals