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Communication

Zeolite micromembranes

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Free-standing silicalite-1 (Sil-1) zeolite micromembranes have been successfully fabricated onto silicon substrate. Gas permeation test using permanent gases (*i.e.*, helium, hydrogen, argon and nitrogen) and hydrocarbons (*i.e.*, methane and n-butane) indicates that the micromembranes have excellent permeance flux and high permselectivity.

Introduction

Zeolites are known for their molecular sieving properties and are capable of separating molecules by their size, shape and polarity.[1,2] This makes zeolites excellent materials for membrane.[3] Zeolites also possess good mechanical strength and thermal stability and are resistant to most acids, bases and organic solvents. In addition, zeolites are known to catalyze many important reactions and can be used for catalytic membranes. Recently, there has been significant interest in zeolite applications for microsystems. Rebrov and coworkers[4] tested a Ce-exchanged ZSM-5 coated stainless steel microchannel reactor (*i.e.*, 500 μm channel width) for selective catalytic reduction of NO by ammonia and den Exter *et al.*[5] described the fabrication of free-standing silicalite-1 film on silicon wafer. The group of Yeung demonstrated different strategies for incorporating zeolites in microchemical systems for use in separations and reactions.[6–8] The 1-pentene epoxidation reaction was successfully conducted in a TS-1 zeolite microreactor.[9]

Aim of investigation

Zeolite micromembranes have applications in separation of gas, gas–liquid and liquid–liquid mixtures. They also find uses as selective barriers for sensors and ion-conducting membranes for electrochemical systems (*e.g.*, micro fuel cells). Miniaturization benefits membrane separation by improving mass and heat transfer rates.[10,11] It also allows a larger membrane area to be packed in a smaller volume, therefore enabling the design of a more efficient and compact separation unit. This work reports the fabrication of a zeolite micromembrane and its performance for gas permeation. Although there are numerous works that discuss the fabrication of zeolite micromembranes, to our knowledge this is the first successful demonstration of gas permeation in zeolite micromembranes.

Experimental

A test element consisting of forty-nine freestanding silicalite-1 micromembranes was fabricated using a new procedure developed in our laboratory. Conventional photolithography and etching techniques were employed to make the 7 × 7 grid pattern on the silicon(100) substrate. The 300 μm squares were etched to a depth of 250 μm. A large 7 mm × 7 mm square was then etched onto the reverse side of the pattern, such that only a thin layer (~50 μm) of silicon separated the two patterns. Localized zeolite growth within the grid patterns was achieved through selective seeding. The grid patterns were functionalized using mercapto-3-propyltrimethoxysilane (50 mM in ethanol) and then seeded with colloidal zeolite (2 wt.% 120 nm TPA–Sil-1 in ethanol) using a micropipette. The seeding procedure was repeated five times to obtain the desired seed population. The seed layer was critical to the secondary growth of the zeolite membrane and could directly affect the zeolite grain size and film orientation. A 5 μm thick Sil-1 film was grown onto the seeded grids from a synthesis solution containing a molar ratio of 40 tetraethylorthosilicate (TEOS) : 10 tetrapropylammonium hydroxide (TPAOH) : 20000 H_2O at 398 K for 48 h. After the zeolite was grown by hydrothermal synthesis, the Sil-1 film was inspected using an optical microscope for defects and imperfections. X-Ray diffraction analysis (Philips PW1030) indicated that a highly oriented (101) Sil-1 film was obtained under these synthesis conditions. The remaining thin layer of silicon that separated the two patterns was then etched and removed in order to expose the free standing Sil-1 film. A leak test of the micromembrane test unit was conducted using helium. Prior to the removal of the organic template molecules (*i.e.*, TPA^+) trapped within the zeolite pores, the micromembranes were impermeable to helium (ΔP = 400 kPa). The micromembrane test unit was activated at low temperature using oxygen plasma treatment (RF = 400 W, 473 K, 20 h). The activated micromembrane test unit was tested for the permeation of helium, hydrogen, argon, nitrogen, methane and n-butane gases at 303 K. The gases were fed to one side of the test unit where the pressure was kept at 115.1 kPa. The flux across the membrane was then monitored and measured at the opposite side at a fixed pressure of 101.3 kPa (*i.e.*, ΔP = 13.8 kPa). After the permeation measurements, the test unit was imaged using optical (Olympus BH-2) and scanning electron microscopes (JEOL JSM6300) in order to characterize the structure of the micromembranes.

Results and discussion

Fig. 1 displays the optical and scanning electron micrographs of the Sil-1 micromembrane test unit. The test unit containing the array of forty-nine zeolite micromembranes is shown in Fig. 1a. It is evident from Fig. 1b that the silicon is completely removed from the zeolite and that the micromembranes are freestanding. Due to the anisotropic etching of Si(100), the membrane area (260 μm × 260 μm) is smaller than the size of the grid. Each micromembrane is supported mainly by the sloping walls of the grid (Fig. 1c). The supported area is about 4.8 times larger than the freestanding membrane area. This along with the well-intergrown zeolite grain structure (Fig. 1d) provide the micromembranes with excellent mechanical strength. Tests conducted on the impermeable micromembranes before their activation showed that the membranes could easily withstand a gas pressure of 500 kPa. Fig. 1d shows that the Sil-1 micromembrane has an average crystal size of 4.4 μm and a thickness of 5 μm (Fig. 1d inset). The excellent intergrowth of

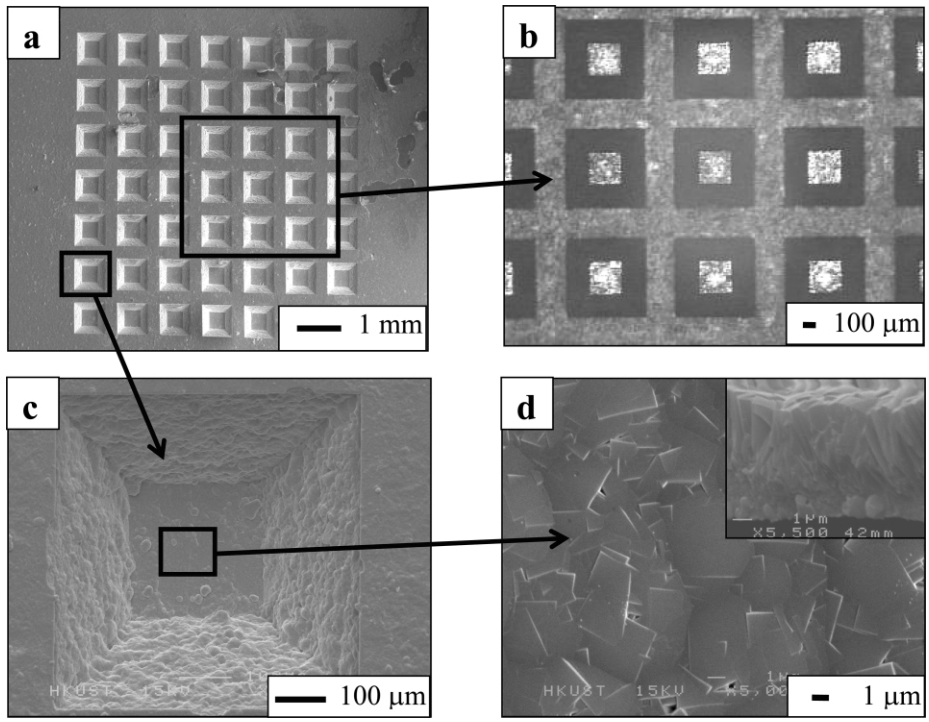

Fig. 1 (a) Optical micrograph of the Sil-1 micromembrane test unit and (b) a higher magnification picture showing the size of the individual micromembranes. Scanning electron micrographs of (c) a single micromembrane and (d) its surface microstructure and cross-section (inset).

the zeolite crystals ensures that the number of non-zeolite transport pathways is kept to a minimum. One of the most critical factors in zeolite membrane preparation is its thermo-mechanical property. The shrinkage in the zeolite crystal during template removal can result in cracks and defects. This was observed in zeolite membranes and films and has even been reported for micron-sized single crystal zeolites.[12] Our strategy is to keep the individual micromembrane area small to prevent stress-related failure and to use oxygen plasma to remove the organic templates at low temperatures. Separate studies showed that template removal by inert gases, diluted oxygen and air at temperatures of 673–823 K led to cracked micromembranes.

Fig. 2 displays the results of the single gas permeation experiment using helium, hydrogen, argon, nitrogen, methane and n-butane gases. Prior to each permeance measurement, the membrane was purged with helium until a reproducible helium flux was obtained. Five permeance measurements were made for each gas, and the entire gas permeation experiment was repeated three times. This provided 15 permeance data points for each gas, which were averaged and plotted as a function of the relative size of the diffusing molecule (*i.e.*, ratio of kinetic diameter d_m to the average zeolite pore diameter d_p). The plot shows that the permeance of hydrogen is the highest, followed by helium, methane, nitrogen, argon, with n-butane being the slowest. The permeance across the micromembranes is higher compared to that of similar supported zeolite membranes of comparable thickness.[3,13] Three transport mechanisms have been identified for zeolites, they are bulk, Knudsen and configurational diffusions. Transport through macroscopic cracks and defects is mainly by bulk diffusion and the expected permselectivity is low. The diffusion of small molecules through the zeolite pores as well as micropores created by intercrystalline grain boundaries and imperfections is primarily Knudsen. But as the size of the diffusing molecules approaches the zeolite pore diameter, configurational diffusion becomes important. The experimental results indicate that the diffusion of small molecules such as hydrogen and helium is Knudsen with a permselectivity (*i.e.*, calculated from the ratio of the single gas permeances) of 1.6, which is close to the expected Knudsen value of 1.4. The He/Ar and He/N_2 ratios of 2.3 and 1.8 are smaller than the calculated Knudsen values of 3.2 and 2.6, reflecting the interactions between the diffusing molecule

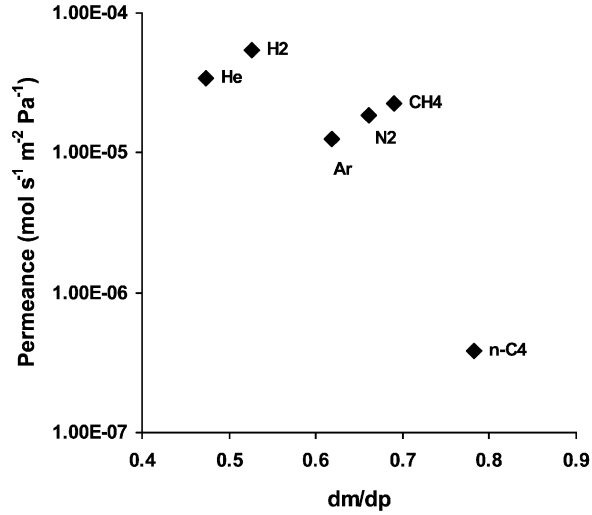

Fig. 2 A plot of single gas permeance as a function of the relative size of the diffusing molecule (*i.e.*, kinetic diameter d_m) to the average zeolite pore diameter (d_p).

and the pore wall.[14] The high permselectivity ratios of hydrogen to the hydrocarbons (H_2/CH_4 = 2.4, H_2/n-C_4 = 140 and CH_4/n-C_4 = 58.7) are due to the restricted movement of the large hydrocarbon molecules through the narrow pore channels. The separations of these latter organic compounds are of economic importance and demonstrate the potentials of membrane microseparator for industrial applications.

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