Journal of Membrane Science 489 (2015) 270–274

Contents lists available at ScienceDirect

Journal of Membrane Science

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

A simple method for blocking defects in zeolite membranes

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ARTICLE INFO

Article history:
Received 19 November 2014
Received in revised form
25 February 2015
Accepted 11 April 2015
Available online 29 April 2015

Keywords:
MFI membrane
Defects
Amorphous Silica
Modification
Gas separation

ABSTRACT

The abatement of defects in zeolite membranes is essential for achieving high selectivity. In the present work, a simple and effective method for blocking defects in ultra-thin (ca. 0.5 μm) MFI zeolite membranes has been developed. The method is based on deposition of an ultra-thin (~15 nm) layer of amorphous silica on the top surface of the membrane. Permporometry data indicated that the amount of defects, especially defects larger than 4 nm, in the membranes was significantly reduced after the modification. In mixture separation experiments, the CO_2/H_2 separation factor increased dramatically after blocking the defects in a defective membrane that was selected for the experiments. For instance, at 263 K and 9 bar feed pressure, the CO_2/H_2 separation factor increased from 8.5 to 36 after modification of the membrane, whereas the CO_2 flux only decreased by ca. 40%.

1. Introduction

Zeolite membranes are considered as promising candidates for a variety of gas separations because of high thermal, chemical and mechanical stability compared to polymeric membranes. However, the presence of defects, especially flow-through defects in the membranes can result in reduced separation performance. Therefore, the elimination of defects is of crucial importance.

Zeolite membranes grow by competitive growth [1], and grain boundaries inevitably form between the grains. We have recently shown [2] that these grain boundaries result in defects in the form of micropores larger than the zeolite pores in the membranes. These grain boundary defects, and also cracks may form during removal of templating agents during calcination [3]. Many zeolite membranes studied in the past have most likely contained defects, which has led to a different membrane performance, underestimation of selectivity, and overestimation of permeance.

In order to reduce the amount of defects in inorganic membranes, several post-synthesis modification procedures have been developed. In mesoporous silica membranes, the pore size was reduced by catalysed atomic layer deposition (C-ALD) [4]. The defects were healed, and self-limited pore size reduction occurred as well. In a study by Lee et al. [5], Pd particles were deposited on microporous silica membranes via a vacuum-impregnation method. It was found that Pd-particle deposition led to improvement of hydrogen permselectivity over nitrogen and, in addition, defects, such as pinholes or cracks, were plugged. For zeolite membranes, selective sealing of cracks in MFI membranes with a surfactant-templated silica sol was examined [6]. Using this method, *p*-xylene/*o*-xylene separation factor was significantly improved up to 30–300. Zhang et al. [7] observed that CO_2/CH_4 selectivity of SAPO-34 membranes increased after treatment with cyclodextrin. These cyclic oligosaccharides were used to fill intercrystaline defects in SAPO-34 membranes. The CO_2/CH_4 selectivity was found to increase by 150% and the CO_2 permeance decreased by 22%.

Selective defect-patching in zeolite membranes has been carried out by a counterdiffusion chemical liquid deposition (CLD) technique [8]. After reparation, the CO_2/N_2 separation factor increased from 1 to 15, and the *n*/*i*-butane separation factor increased from 4.4 to 35.8. Nomura et al. [9] applied a TEOS-O_3 counterdiffusion chemical vapour deposition (CVD) method to silicalite membranes. The CVD-modified silicalite membrane displayed a *n*/*i*-butane gas selectivity of 87.8 after modification. Post-synthesis defect plugging with PDMS in microporous silica and zeolite Y membranes has been performed [10]. After application of PDMS, H_2/CO_2, CO_2/N_2 and CO_2/CH_4 gas selectivities were found to be considerably enhanced. However, low resistance to contaminants, physical aging and membrane plasticisation at high pressures of CO_2 are the general disadvantages of polymeric layers [11]. It should also be pointed out that membranes described above

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http://dx.doi.org/10.1016/j.memsci.2015.04.038
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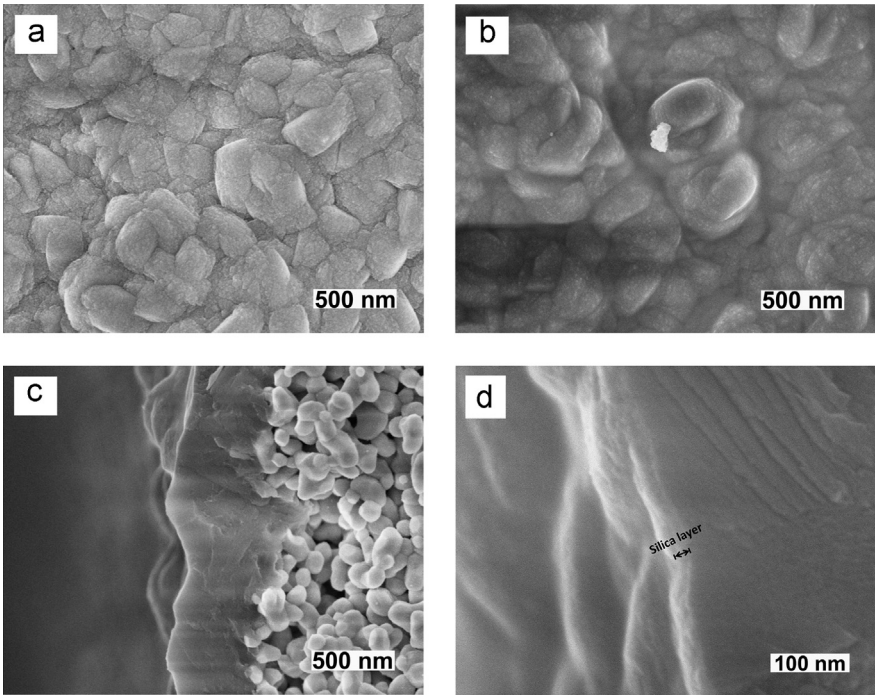

Fig. 1. (a) Top view of an MFI membrane before modification; (b) Top view of the MFI membrane after modification; (c) Cross-sectional view of the MFI membrane after modification; (d) Cross-sectional view recorded at high magnification of the MFI membrane after modification.

displayed CO_2 permeances below 10^{-6} mol s^{-1} m^{-2} Pa^{-1}, which is probably insufficient for many commercial applications. There is thus an urgent need to develop modification methods suitable for membranes with high permeance. Furthermore, it is an advantage if the modification material is an inorganic material, to preserve the inorganic nature of the membrane.

In the present work, ultra-thin MFI membranes were coated with an ultra-thin layer of inorganic silica nanoparticles in order to reduce the flow through defects in the membrane. The morphology of the ultra-thin silica layer deposited on the modified membrane was characterised by SEM. The amount of defects in the membranes before and after the modification was examined by permporometry. In addition, CO_2/H_2 separation performance of the membranes before and after modification was studied. The findings demonstrated that the modification method was effective for blocking defects in MFI membranes and improving the membrane separation performance, while keeping the flux of the modified membranes high.

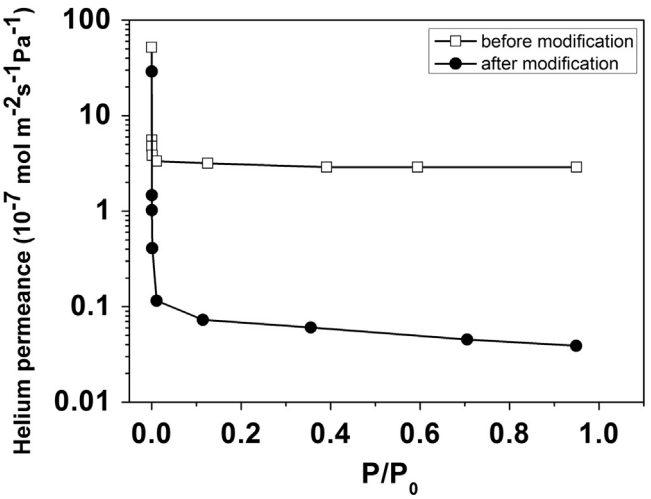

Fig. 2. He permeance through membrane M1 before and after modification as a function of relative pressure of *n*-hexane.

2. Experimental

2.1. MFI membrane synthesis

Our research group [12] has developed high flux ultra-thin (ca. 0.5 μm) MFI membranes with a Si/Al ratio of 139 on α-alumina supports. The detailed preparation procedure is described elsewhere [12] and in brief below. A graded porous α-alumina disc (Fraunhofer IKTS, Germany) was used as a support. The support with a diameter of 25 mm is comprised of a 30 μm thick top layer with a pore size of 100 nm and a 3 mm thick base layer with a pore size of 3 μm. Prior to the film synthesis, the alumina discs were masked and seeded as described in our earlier work [13]. The seeded support was immersed in a synthesis solution with a molar composition of 3 TPAOH:25 SiO_2:1450 H_2O:100 C_2H_5OH and heated in an oil bath kept at 361 K for 72 h, with reflux of evaporated solution. Afterwards, the membrane was rinsed in a 0.1 M NH_3 solution overnight and calcined at 773 K for 6 h, with a heating rate of 0.2 K min^{-1} and a cooling rate of 0.3 K min^{-1}.

2.2. Modification of MFI membrane

The calcined MFI membranes were modified by dipping in a polymeric silica dip solution, followed by drying and calcination. The method developed for modification of the zeolite membranes in the present work is, in principle, a combination of methods developed for preparation of silica membranes [14,15], although with some adaptations. The silica sol was prepared by the sol–gel method. A mixture of nitric acid and distilled water was added to a mixture of tetraethyl orthosilicate (TEOS) and ethanol under vigorous stirring. During the addition of the acid/water mixture, the TEOS/ethanol mixture was kept in an ice-bath to avoid partial hydrolysis. This reaction mixture with a molar composition of