

Zeolite-in-metal Membranes: Preparation and Testing

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By galvanic metal deposition, silicalite crystals have been embedded in silver or nickel foils; the resulting composites are self-supporting high-temperature membranes (thermally stable up to 650 K) and have been tested by permeation/pervaporation studies of a binary *n*-heptane–toluene mixture; a separation factor $\alpha_{\text{tol}/n\text{-C7}}$ ca. 4 ± 1.5 is found over a wide temperature range.

During the last few years, increasing attempts have been made to develop zeolite membranes for separation and catalysis applications, *e.g.* the crystallisation of thin continuous zeolite films on a mesoporous ceramic,^{1a,b,c} metal^{1d} or glass^{1e} support, the preparations of self-supporting ZSM-5,^{2a-d} zeolite A^{2e} and SAPO^{2f} films and the embedding of zeolite crystals in a zeolite–silica or alumina micro-composite film.³ In this paper we present a novel type of a high-temperature membrane obtained by the electrochemical embedding of zeolite crystals in a metal matrix.⁴

The membranes were produced as follows. Using a centrifuge, by spin coating, a few μm -thick film of an electrically-conducting silver lacquer was deposited on a glass plate used as a plane support. Then silicalite crystals (the practically Al-free form of ZSM-5, *cf.* Fig. 1) were brought with perforated matrices on this sticky film. Then the glass support with the fixed crystals was used as a cathode in a galvanic silver or nickel bath. The metal film grew exclusively between the crystals, directly on the conductive lacquer. When the metal

film reached the top level of the crystals, electrolysis was stopped and the metal film with the embedded crystals was removed from the glass support by a solvent for the conducting lacquer (*e.g.* acetone). Fig. 1 shows a cross-section through the silicalite-in-silver membrane. Fig. 2 gives an impression of a silicalite-in-nickel-membrane with silicalite crystals oriented vertically. The alignment of the crystals has been achieved as described in *ref.* 5 by electric field.

The state-of-the-art of preparing such zeolite-in-metal membranes is characterised by the fact that at present the embedding of crystals with sizes $\geq 20 \mu\text{m}$ in a metal foil is under control. About 15% of the surface can be made transport active, *i.e.* covered with zeolites.

The results presented here were obtained on a membrane with 489 silicalite crystals of $30 \times 30 \times 80 \mu\text{m}$ size horizontally oriented which give—under consideration of the partial

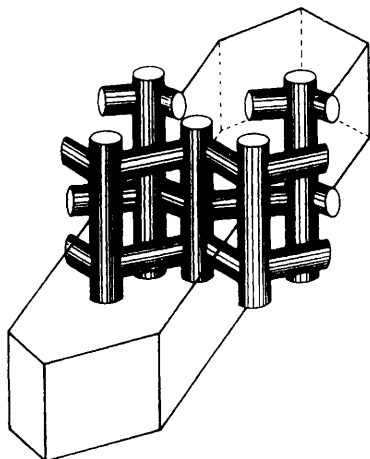
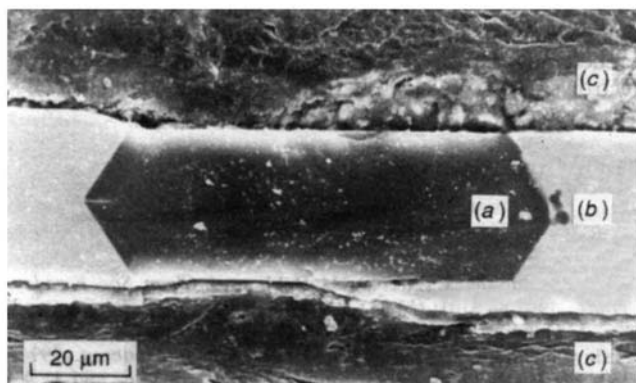


Fig. 1 SEM image of a cross section of the silicalite-in-metal membrane with: (a) the embedded ZSM-5 crystal, (b) the silver film. (c) Denotes epoxy resin which has been used to stabilize the foil to enable perpendicular abrasion. The relation between the pore system and the crystal shape is shown schematically: straight channels of elliptical cross sections ($5.1 \times 5.4 \text{ \AA}$) are cross-linked by sinusoidal channels of nearly circular cross section (5.4 \AA)

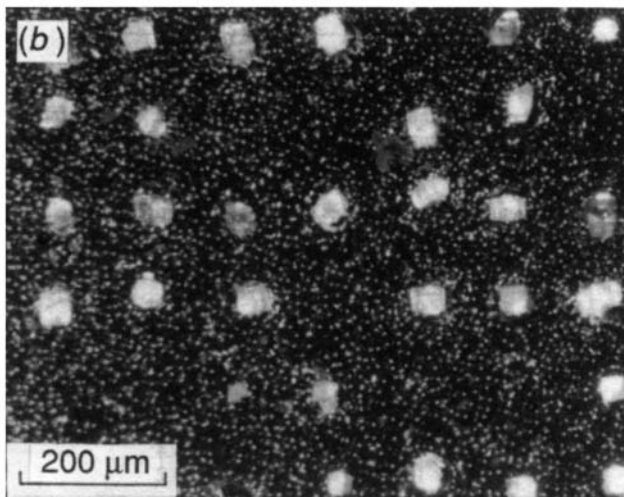
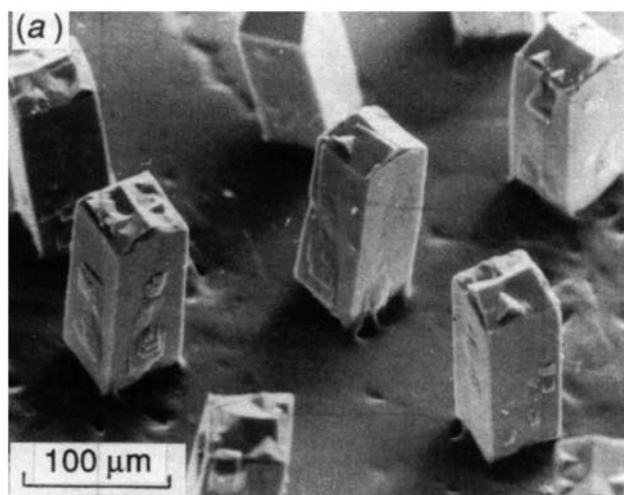


Fig. 2 (a) Vertically oriented silicalite crystals attached to an Ag lacquer which conducts electricity. (b) Is a transmission light microscopic picture of the membrane after electrolysis. Every light spot corresponds to an ZSM-5 crystal embedded vertically in the Ni foil

overgrow—a net zeolite area of $8.7 \times 10^{-3} \text{ cm}^2$ for permeation.

The perfection of the membrane, *i.e.* the absence of pin-holes, has been tested by several methods: (i) the pure metal film without any embedded particles was absolutely gas-tight; (ii) also zeolite-in-metal membranes with silicate crystals still containing the tetrapropylammonium ions (used as a template in the ZSM-5 synthesis) were gas-tight. The template molecules are trapped in the channel intersections of the ZSM-5 pore system thus preventing any gas transport through the embedded crystal. (iii) Zeolite-in-metal membranes containing calcinated crystals were tested with SF_6 which is too bulky to enter the 5.5 \AA pores of silicalite. Only membranes which are practically unpermeable for SF_6 have been used in the following permeation studies of hydrocarbons.

On the feed side of the membrane was either the liquid (pervaporation) or evaporated (permeation) binary *n*-heptane–toluene 1:1 (in mass) mixture at 1 bar. The permeate side was evacuated and the permeate was frozen out. Therefore, a constant pressure difference of 1 bar across the membrane can be assumed. Since *n*-heptane and toluene are

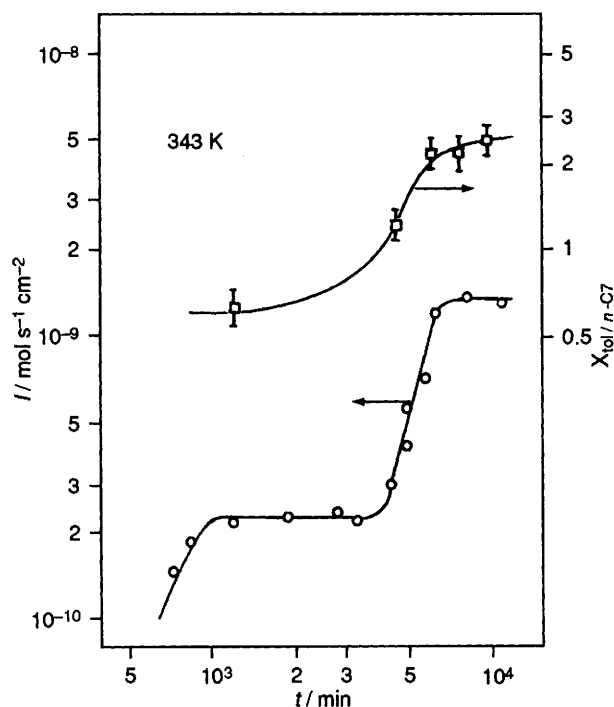


Fig. 3 Integral permeation flux density $I_{\Sigma, \text{mixt}}$ and the separation factor $\alpha_{\text{tol}/n\text{-C7}}$ as function of time

Table 1 Permeation flux densities $I_{\Sigma, \text{mixt}}$, permeation coefficients $P_{\Sigma, \text{mixt}}$ and separation factors $\alpha_{\text{tol}/n\text{-C7}}$

T/K	$I_{\Sigma, \text{mixt}}/\text{mol cm}^{-2} \text{ s}^{-1} \text{ a}$	$P_{\Sigma, \text{mixt}}/\text{mol (cm s bar)}^{-1} \text{ b}$	$\alpha_{\text{tol}/n\text{-C7}} \text{ c}$
323	1.2×10^{-9}	3.6×10^{-12}	5.0
343	6.6×10^{-9}	2.0×10^{-11}	2.6
364	2.0×10^{-8}	6.0×10^{-11}	3.3
383	4.3×10^{-8}	1.3×10^{-10}	3.3
413	3.0×10^{-8}	9.0×10^{-11}	5.4
443	4.3×10^{-8}	1.3×10^{-10}	4.2

^a Ratio of the total flux (both components) and the effective membrane area. ^b Obtained by dividing $I_{\Sigma, \text{mixt}}$ by the pressure difference of 1 bar over the membrane, and multiplying by the crystal thickness of $30 \mu\text{m}$. ^c From gas-chromatographic analysis of the permeate.

of almost the same molecular mass, any deviation of the separation factor from 1 has to be taken as a straightforward indication that mass transport is governed by zeolite diffusion and not by a Knudsen mechanism through pin-holes or other defects. Further evidence for the zeolitic properties of the membrane follows from the ratio of the fluxes of the hydrocarbons and SF_6 . For perfect membranes, this ratio was always found to be close to infinity. For a non-zeolitic transport, however, this ratio should be equal to the ratio of the molecular masses, *i.e.* equal to $\sqrt{(\text{C}_7\text{H}_{16}/\text{SF}_6)} \approx 0.8$.

The permeation measurements were carried out in a temperature range from 323 to 443 K. As an example, Fig. 3 shows the net permeation flux density $I_{\Sigma, \text{mixt}}$ and the separation factor $\alpha_{\text{tol}/n\text{-C7}}$ at 323 K as a function of the permeation time. For two regions, $I_{\Sigma, \text{mixt}}$ remains constant, *i.e.* in these two regions we have an almost linear pressure increase caused by (i) the *n*-heptane breakthrough, and (ii) later the steady state permeate which is enriched in toluene (*c.f.* Fig. 3), respectively. The increase in $\alpha_{\text{tol}/n\text{-C7}}$ is linked to an increase of $I_{\Sigma, \text{mixt}}$ until steady state is reached. Note that the first $\alpha_{\text{tol}/n\text{-C7}}$ value is < 1 , *i.e.* in the beginning of permeation the permeate is enriched in *n*-heptane (the molecule with the higher diffusivity). As Table 1 shows, the $\alpha_{\text{tol}/n\text{-C7}}$ data show no regular trend with the temperature and amount to 4 ± 1.5 .

The importance of this study, however, is not in flux densities or selectivities obtained on the binary model system, but finding that it is possible to manufacture a pin-hole-free molecular sieve membrane for separation and catalytic purposes at elevated temperatures by a simple galvanic process⁴.

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