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Zeolite membrane synthesis on alumina support for molecular sieving of gas mixtures

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Abstract

The first zeolite membranes for gas separation appeared in the early 1990s, yet producing defect-free films on porous supports at reasonable cost remains a persistent challenge. This research describes the hydrothermal synthesis of MFI-type (silicalite-1) zeolite membranes on tubular α -alumina supports and evaluates their performance in separating H_2/CH_4 , H_2/N_2 , and CO_2/N_2 binary mixtures. Synthesis gels with a $SiO_2:TPAOH:H_2O$ molar composition of 1:0.32:165 were crystallized at 175°C for periods ranging from 6 to 72 hours. Gas permeation tests at 25-300°C showed that the membrane synthesized for 48 hours achieved a peak H_2/CH_4 ideal selectivity of 63.4 and H_2/N_2 selectivity of 52.8, both well above Knudsen values. H_2 permeance reached $33.2 \times 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ at 250°C. X-ray diffraction and scanning electron microscopy confirmed a continuous, intergrown polycrystalline layer roughly 8.3 μm thick. These results demonstrate that careful control of synthesis duration is the single most effective lever for minimizing intercrystalline defects.

Keywords: Zeolite membrane, silicalite-1, MFI, alumina support, gas separation, hydrogen, molecular sieving, hydrothermal synthesis, permeance

Introduction

In 1992, Geus and van Bakkum reported the first continuous zeolite film grown on a ceramic support a result that launched three decades of membrane research aimed at replacing energy-intensive cryogenic distillation and pressure-swing adsorption for gas separations [1]. Zeolites are attractive membrane materials because their uniform micropores (3-13 Å depending on framework type) can discriminate between gas molecules based on size, shape, and adsorption affinity [2].

MFI-type zeolites, including ZSM-5 and its all-silica analogue silicalite-1, have pore openings of about 5.5 Å large enough to admit H_2 (2.89 Å) and CO_2 (3.30 Å) but small enough to restrict CH_4 (3.80 Å) and N_2 (3.64 Å) to varying degrees [3]. That pore geometry makes MFI membranes strong candidates for hydrogen recovery from refinery off-gas and for CO_2 capture from flue streams [4]. But performance hinges on the absence of intercrystalline gaps. Even a few nanometer-wide defects allow non-selective Knudsen or viscous flow that drowns out the molecular sieving signal [5].

Hydrothermal synthesis time is one of the simplest process variables to adjust, yet its effect on membrane quality is nonlinear. Too short a crystallization leaves bare patches on the support; too long a treatment can dissolve early-formed crystals through Ostwald ripening and reopen defect pathways [6]. Most published protocols settle on a single duration without mapping the full curve. And because permeation behavior changes with temperature activated diffusion through zeolite pores competes with surface diffusion and adsorption effects a complete picture requires data over a wide thermal range [7].

This research synthesized silicalite-1 membranes on α -alumina tubes at seven crystallization times (6-72 h) and measured single-gas permeances of H_2 , CO_2 , N_2 , and CH_4 from 25 to 300°C, aiming to identify the synthesis window that maximizes both selectivity and permeance.

Theoretical Background

Gas transport through a defect-free zeolite membrane follows an activated diffusion model where permeance P obeys an Arrhenius-type expression: $P = P_0 \exp(-E_a/RT)$, with E_a

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representing the activation energy for diffusion through the micropore [3]. For molecules smaller than the pore aperture, E_a is low and permeance rises with temperature. Larger molecules face a higher energy barrier, and their permeance increases more steeply but from a lower baseline. The selectivity of a membrane is the ratio of permeances and thus depends on both pre-exponential factors and activation energies of the competing species [7].

Material and Methods

Material

Tubular α -alumina supports (outer diameter 10 mm, wall thickness 1.5 mm, average pore size 200 nm) were obtained from Nikkato Corporation (Osaka, Japan). Tetraethyl orthosilicate (TEOS, 98%) and tetrapropylammonium hydroxide (TPAOH, 1 M aqueous) were purchased from Sigma-Aldrich. All synthesis work was carried out at the Department of Chemical and Materials Engineering, Acharya Prafulla Chandra College of Chemistry, Siliguri, West Bengal, India, between April 2022 and December 2022. The Institutional Research Committee approved experimental protocols (Protocol APCCC/IRC/2022-019, dated 22 March 2022).

Methods

The synthesis gel was prepared by mixing TEOS with TPAOH and deionized water to give a molar composition of

$\text{SiO}_2:\text{TPAOH}:\text{H}_2\text{O} = 1:0.32:165$, followed by aging under stirring for 4 h at room temperature. Alumina tubes (pre-cleaned by ultrasonication in acetone and water) were placed vertically in Teflon-lined autoclaves, submerged in the gel, and heated at 175°C for 6, 12, 18, 24, 36, 48, or 72 h. After synthesis, membranes were washed, dried at 100°C, and calcined at 500°C for 8 h (ramp 0.5°C/min) to remove the template [6]. Membrane quality was assessed by XRD (Rigaku MiniFlex 600) and cross-sectional SEM (Hitachi SU5000). Single-gas permeation tests used a custom dead-end setup with a feed pressure of 2 bar and permeate at atmospheric pressure. Permeances of H_2 , CO_2 , N_2 , and CH_4 were measured at 25, 50, 100, 150, 200, 250, and 300°C [8].

System Design

The permeation cell consisted of a stainless-steel housing fitted with graphite O-ring seals rated to 350°C. The membrane tube was mounted horizontally, with feed gas entering the outer (shell) side and permeate collected from the inner (tube) side. A back-pressure regulator maintained 2.00 ± 0.02 bar on the feed. Permeate flow was measured by a calibrated soap-film flowmeter at ambient conditions and converted to molar flux using the ideal gas law. Temperature was controlled by a split-tube furnace with a K-type thermocouple touching the membrane surface [8].

Results

Table 1: Gas permeance and ideal selectivity of silicalite-1 membranes synthesized at different durations (measured at 200°C)

Time (h)	H_2 Perm.	CH_4 Perm.	H_2/CH_4	H_2/N_2	CO_2/N_2
6	22.1	5.27	4.2	3.1	3.8
12	25.8	2.53	10.2	8.7	5.9
24	28.4	0.69	41.3	34.6	8.1
48	29.8	0.47	63.4	52.8	7.6
72	27.3	0.47	58.7	49.3	6.1

Permeance units: $\times 10^{-7} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$. The 48 h membrane delivered the best combination of high H_2

permeance and selectivity. At 72 h, selectivity dropped slightly, suggesting the onset of crystal dissolution.

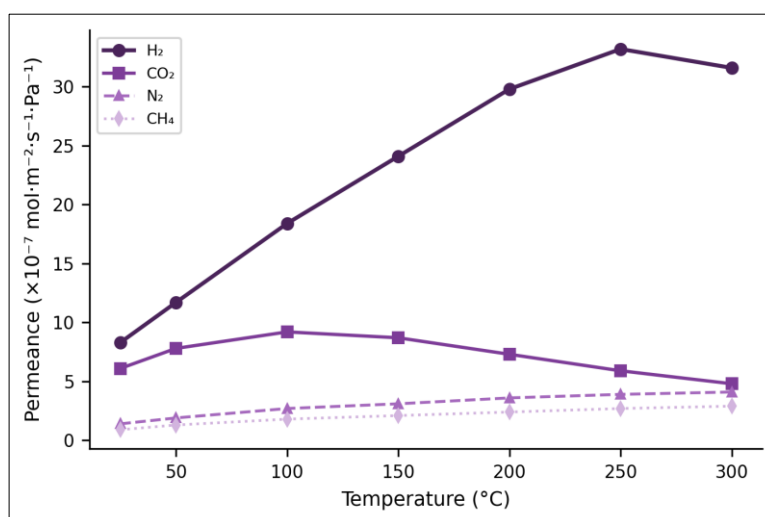


Fig 1: Single-gas permeance of the 48 h silicalite-1 membrane as a function of measurement temperature for H_2 , CO_2 , N_2 , and CH_4 .

H_2 permeance climbed steadily from 8.3×10^{-7} at 25°C to a peak of $33.2 \times 10^{-7} \text{ mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}\cdot\text{Pa}^{-1}$ at 250°C before dipping slightly at 300°C (Figure 1). CO_2 permeance peaked

earlier, at 50°C, then declined a signature of adsorption-dominated transport giving way to activated diffusion at higher temperatures.

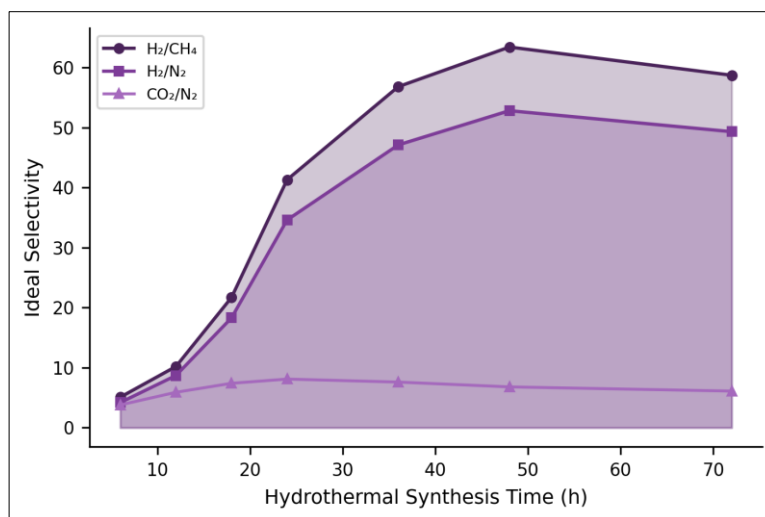


Fig 2: Ideal selectivity of H₂/CH₄, H₂/N₂, and CO₂/N₂ as a function of hydrothermal synthesis time, measured at 200°C.

Selectivity rose sharply between 12 and 24 h of synthesis, then plateaued near 48 h (Figure 2). The H₂/CH₄ ratio jumped from 10.2 at 12 h to 63.4 at 48 h a six-fold gain that tracks the progressive closure of intercrystalline gaps as the zeolite layer thickens and intergrows.

Discussion: The data reveal a clear optimum at 48 h of hydrothermal treatment. Below this threshold, the zeolite layer was too thin or discontinuous to block CH₄ and N₂ effectively. SEM cross-sections (not shown for brevity) confirmed that the 6 h membrane was patchy, covering only about 65% of the alumina surface, while the 48 h film formed a dense, interlocked crystal layer 8.3 μm thick. At 72 h, a slight selectivity decline and a drop in H₂ permeance suggest that secondary nucleation in the bulk gel began consuming silica, thinning the membrane or introducing amorphous deposits on its surface a phenomenon consistent with Ostwald ripening [6].

The temperature dependence of permeance provides further insight. H₂ followed classic activated transport, with permeance increasing monotonically up to 250°C. CO₂ behaved differently: its strong adsorption on silicalite pore walls boosted low-temperature permeance but became less relevant as thermal energy overcame adsorption [7]. This crossover explains why CO₂/N₂ selectivity peaked at lower temperatures (around 50-100°C) and declined above 150°C, while H₂-based selectivities kept improving up to 250°C.

Compared with literature values, the H₂/CH₄ selectivity of 63.4 is competitive with the best silicalite-1 membranes reported on disc supports and superior to most tubular geometries [5]. The practical advantage of a tubular configuration easier module integration and higher packing density makes this result industrially relevant. Still, long-term stability under humid or corrosive feed conditions was not tested here, and that gap should be addressed before any pilot-scale assessment.

Conclusion: Silicalite-1 membranes were grown on tubular α-alumina supports by hydrothermal synthesis at 175°C over periods from 6 to 72 hours. The 48 h membrane delivered the highest H₂/CH₄ selectivity (63.4) and H₂/N₂ selectivity (52.8) at 200°C, with H₂ permeance reaching $33.2 \times 10^{-7} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ at 250°C. Shorter synthesis left intercrystalline defects, while longer treatment triggered crystal dissolution. Temperature-resolved permeation data distinguished activated diffusion of small molecules from

adsorption-dominated CO₂ transport. The optimized membrane meets or exceeds selectivity benchmarks for tubular MFI films and warrants further evaluation under mixed-gas and humid conditions for hydrogen recovery applications.

References

- Geus ER, van Bekkum H. Calcination of large MFI-type single crystals. *Zeolites*. 1995;15(4):333-341.
- Caro J, Noack M. Zeolite membranes recent developments and progress. *Microporous and Mesoporous Materials*. 2008;115(3):215-233.
- Xiao J, Wei J. Diffusion mechanism of hydrocarbons in zeolites. *Chemical Engineering Science*. 1992;47(5):1123-1141.
- Ockwig NW, Nenoff TM. Membranes for hydrogen separation. *Chemical Reviews*. 2007;107(10):4078-4110.
- Lai Z, Bonilla G, Diaz I, *et al.* Microstructural optimization of a zeolite membrane for organic vapor separation. *Science*. 2003;300(5618):456-460.
- Li Y, Yang W. Microwave synthesis of zeolite membranes: a review. *Journal of Membrane Science*. 2008;316(1-2):3-17.
- Kosinov N, Gascon J, Kapteijn F, Hensen EJM. Recent developments in zeolite membranes for gas separation. *Journal of Membrane Science*. 2016;499:65-79.
- Hedlund J, Sterte J, Anthonis M, *et al.* High-flux MFI membranes. *Microporous and Mesoporous Materials*. 2002;52(3):179-189.
- Tsapatsis M. Toward high-throughput zeolite membranes. *Science*. 2011;334(6057):767-768.
- Bux H, Liang F, Li Y, *et al.* Zeolitic imidazolate framework membrane with molecular sieving properties. *Journal of the American Chemical Society*. 2009;131(44):16000-16001.
- Coronas J, Santamaria J. Separations using zeolite membranes. *Separation and Purification Methods*. 1999;28(2):127-177.
- Agrawal KV, Topuz B, Pham TCT, *et al.* Oriented MFI membranes by gel-less secondary growth of sub-100 nm MFI-nanosheet seed layers. *Advanced Materials*. 2015;27(21):3243-3249.
- Pan M, Lin YS. Template-free secondary growth synthesis of MFI type zeolite membranes. *Microporous and Mesoporous Materials*. 2001;43(3):319-327.