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Preparation and characterization of Pd-zeolite composite membranes for hydrogen separation

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Abstract

Zeolite A membranes have been synthesised by secondary growth on the surface of macroporous α -alumina and stainless steel tubular supports, previously seeded with zeolite A crystals. The membranes thus obtained were used in the separation of H_2/N_2 and H_2/C_3H_8 mixtures. Stainless steel supports appeared to be more adequate for the development of zeolite A membranes by secondary growth, as evidenced by the results of XRD analysis and by higher values of selectivity and gas permeance obtained. The resulting membranes were further modified by CVD of a Pd compound or impregnation with a Pd salt solution, in order to minimize the non-selective defects by Pd deposition. Permeation measurements carried out under pressure gradient did not show any apparent beneficial effect of Pd over H_2/N_2 separation. However, in permeation tests carried out using a sweep gas, higher separation factors were achieved (e.g., ideal selectivity H_2/C_3H_8 of 17.35 at 323 K, and H_2/C_3H_8 separation factor of 7.28 at the same temperature).

Keywords: Zeolite NaA; Membrane; Palladium deposition; Hydrogen separation

1. Introduction

Supported zeolite membranes have been extensively developed over the last two decades due to their potential applications in membrane separators, membrane reactors and selective sensors. This is due to the intrinsic properties of zeolites and the advantages of a membrane-type

configuration. Zeolites are microporous crystalline materials with a uniform pore size distribution in the molecular size range. The molecular sieving properties of these materials proclaims them as excellent candidates for separation applications; however, a continuous and nearly defect-free zeolite layer is required for good performance of the membrane separation system.

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A-type zeolite membranes (channel opening size of 0.41 nm for NaA zeolite and 0.35 nm for KA zeolite) offer excellent prospects for the separation of permanent gases or of mixtures of permanent gases and organic vapours, in particular for the separation of hydrogen from hydrocarbon mixtures. Various processes for production and purification of hydrogen have attracted much attention world-wide [1] because hydrogen is emerging as an important energy resource to meet environmental requirements. Because of their small pore size, zeolite A membranes could be a competitive alternative for H₂ separation. However, some difficulties arise with this approach because a negligible concentration of inter-crystalline defects is required for good separation performance. The probability of defects increases with membrane dimensions and the synthesis of sufficiently large membrane structures with a low concentration of defects remaining the main obstacle for gas separation applications. The relatively few gas permeation studies reported for this type of zeolite [2–8] show that in general defective zeolite membranes are obtained, even when synthesised on disk supports. Still, very good performance can be obtained in liquid-phase applications, as shown by pervaporation studies [9] where competitive adsorption rather than molecular sieving is the dominant separation mechanism.

A successful membrane formation in one-process (direct) membrane synthesis requires preferential nucleation and growth of zeolite crystals on the support surface, which competes with solution events. An alternative approach for zeolite membrane formation is the technique referred to as secondary (seeded) growth, which involves a first step in which a closely packed layer of zeolite seed crystals is deposited onto the surface of a support. These seeds act as nuclei for further crystal growth that, under suitable hydrothermal conditions, should fill the inter-crystalline voids. The production of a relative thin and continuous zeolite film coating is more

difficult for systems containing large Al/Si ratios, a problem for the synthesis of zeolite A membranes where this ratio is around 1. In this work, Pd deposition on already prepared zeolite A membranes has been used in an attempt to block inter-crystalline defects while maintaining H₂ permeation capability.

2. Experimental

2.1. Membrane preparation

Zeolite membranes were hydrothermally synthesised on the surface of tubular supports. Two types of porous supports were used for zeolite membrane preparation: (a) α -alumina symmetric tubes of 7 mm ID, 10 mm OD, with a nominal pore size of ~1900 nm (Inocermic); and (b) stainless steel tubes of similar dimensions with an effective pore size of ~500 nm (Mott Metallurgical). Zeolite A crystals with a mean size of 1 μ m were used as seed in both cases. Two seeding procedures were used, namely, rubbing of zeolite crystals on the membrane surface and cake filtration of an aqueous suspension of zeolite crystals (0.5% wt). Secondary growth of the seed layer deposited on the support tubes was carried out hydrothermally for 5 h at 80°C with a clear solution prepared according to the recipe given by Kumakiri et al. [10].

2.2. Palladium deposition

Two different methods were used to deposit palladium over zeolite A membranes. The first involved a prolonged chemical vapour deposition (CVD) of a commercial metal-organic compound, palladium(II) acetylacetonate, termed Pd(acac)₂ in this work. The Pd(acac)₂ vapours coming from the sublimation chamber contacted the membrane outer (zeolite layer) side, while maintaining the permeate side at a moderate vacuum (1 mbar). They adsorbed on the zeolite layer where they reacted and decomposed at temperatures between 170–200°C.

3. Results and discussion

3.1. Membrane characterization

Table 1 summarises the main characteristics of the membranes obtained regarding N₂ permeation for the commercial support and the zeolite membrane finally obtained. The percentage of laminar contribution to the N₂ permeance has been evaluated at an average pressure of 1 bar, according to the equation proposed by Keizer et al. [11]. As can be observed, several syntheses were necessary over both types of support to reach suitable permeation levels with a low contribution of Poiseuille flow.

Considering the differences in the support density (three times higher for stainless steel material), the weight loading of zeolite per unit membrane volume is approximately the same. To deposit a layer of seeds suitable for crystal growth, rubbing proved more effective than cake filtration. Thus, sample MA3 presented a permeation of 4.04×10^{-8} mol N₂/m².s.Pa after the fifth synthesis cycle, whereas for MA2 the NA permeance was 2.39×10^{-6} mol/m².s.Pa at the

same stage. Further synthesis cycles (up to 9) were needed, with seeding by external rubbing, to reduce the N₂ permeation flux to 8.87×10^{-8} mol N₂/m².s.Pa.

The surface microanalysis (EPMA) results for membrane MA1 revealed a high concentration of Pd (up to 30 atom %) on the membrane surface exposed to vapours, for a thickness of about 10 μm. For the vacuum with a 0.003 M solution of Pd(acac)₂/acetone. The objective was to increase the palladium loading and to facilitate the growth of Pd nuclei already deposited by CVD inside the zeolite layer. In this case, EMPA analysis revealed a Pd concentration of up to 3.7 atom % on the membrane surface exposed to vapours (10 μm thickness), while for the opposite side a Pd concentration of 2 atom % was detected across the first 50 mm, i.e., inside the macroporous support. For the MSS3 membrane (0.005% Pd loading) prepared by successive impregnations, Pd was also detected inside the macroporous structure of the support (1–1.5 atom %). In these samples, the Si/Al ratio observed by EMPA was around 1–1.7 along the first 30 mm

Table 1

Main characteristics for the different type A zeolite membranes prepared in this work

Membrane ^a	Initial permeation (mol N ₂ /m ² .s.Pa)	Seeding method (seed loading)	No. synthesis NaA-loading ^b	Final permeation (mol N ₂ /m ² .s.Pa)	Pd depos. ^d Loading (%) ^b	% laminar contribution
MSS1	3.18×10^{-5}	External rubbing	5 (3.14 mg/g)	2.94×10^{-8}		14
MSS2	8.84×10^{-5}	External rubbing	7 (2.15 mg/g)	1.02×10^{-7}	B+A 0.05%	10
MSS3	10.6×10^{-5}	External rubbing	8 (2.06 mg/g)	2.13×10^{-7}	A 0.005%	13
MSS4	5.50×10^{-5}	External rubbing	6 (2.19 mg/g)	2.00×10^{-7}		3
MSS5	8.66×10^{-5}	External rubbing	8 (2.24 mg/g)	2.91×10^{-7}		2
MA1	5.00×10^{-5}	External rubbing	3 (9.92 mg/g)	4.86×10^{-8}	B 0.13%	31
MA2	1.41×10^{-5}	Internal filtration ^c	9 (6.24 mg/g)	8.87×10^{-8}		20
MA3	7.15×10^{-5}	External rubbing	5 (9.30 mg/g)	4.04×10^{-8}		0

^aSS indicates stainless steel support and A α-Al₂O₃ support.

^bExpressed per total membrane weight.

^cSeeding by rubbing before 7th, 8th, and 9th hydrothermal synthesis.

^dA = vacuum filtration of a Pd (acac)₂ solution; B = CVD of Pd (acac)₂.

distance to the external surface in agreement with SEM observations of zeolite thickness (Fig. 2); additionally, some zeolite material was also synthesised inside the support.

3.1. Permeation tests for type-A zeolite membranes

The relative few studies found in literature concerning gas separation applications with this type of zeolite membranes are summarised in Table 2. With tubular supports the best results found for gas separation are 5.83 as ideal selectivity for $H_2/n-C_4H_{10}$ (the Knudsen value is 5.38) and 8.33 for an equimolar mixture with a H_2 permeance value of $7 \times 10^{-10} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$ at 473 K [2]. Until now, no highly permselective zeolite A membranes have been reported in gas separation applications. The permeation tests reveal that membranes contain defects larger than the zeolitic pores; through these, large molecules (e.g., $n-C_4H_{10}$ with a kinetic diameter of 4.3 Å)

were able to permeate, explaining the low selectivity (close to the Knudsen values) observed.

Single gas permeation measurements were conducted on the membranes prepared in this work while keeping the retentate at 0.1 barg. The feed was always introduced from the side of the zeolite layer. Table 3 summarises the N_2 , H_2 and SF_6 permeation data estimated at $\Delta P = 0.1$ bar for two representative membranes. With a defect-free membrane, infinite H_2/SF_6 separation factors would be expected, since SF_6 is not able to transit the zeolite pore network. However, for H_2/N_2 mixtures where the size of both components is smaller than the zeolite pores, the selectivities would be similar to Knudsen values, given the diffusivities quoted for light gases over 4A zeolites [12]. The N_2 permeances obtained are on the same order of magnitude as those found in literature with the exception of ones reported by Aoki et al. [2]. The ideal selectivity calculated as the ratio of single gas permeances at $\Delta P = 0.1$

Table 2

Summary of properties for zeolite A membranes previously used in gas permeation studies

Ref.	Synthesis characteristics			Single gas permeances ($\text{mol/m}^2 \cdot \text{s} \cdot \text{Pa}$)		
	Support	Synthesis conditions	Gel molar ratio Na:Al:Si:H ₂ O	H ₂	N ₂	n-C ₄ H ₁₀
[2]	α -Al ₂ O ₃ tube	Secondary growth 100°C–20 h	2:1:1:240	6.5×10^{-10} (308 K)	5×10^{-10} (308 K)	1.2×10^{-10} (308 K)
[3]	α -Al ₂ O ₃ tube	Secondary growth 100°C–3 h	2:1:1:120	1.04×10^{-7} (378 K)	3.95×10^{-7} (378 K)	
[4]	α -Al ₂ O ₃ disk	Secondary growth 90°C–24 h	3:1:1:100	3.0×10^{-7} (298 K) 4.0×10^{-7} (423 K)	1.5×10^{-8} (298 K) 2.0×10^{-8} (423 K)	3.0×10^{-9} (298 K) 6.0×10^{-9} (423 K)
[5]	α -Al ₂ O ₃ disk	Secondary growth 90°C–4 h	100:2:5:1000	8.76×10^{-7} (298 K) 2.13×10^{-6} (298 K)*	2.77×10^{-7} (298 K) 6.66×10^{-7} (298 K) ^a	2.22×10^{-7} (298 K) 1.79×10^{-7} (298 K) ^a
[6]	α -Al ₂ O ₃ disk	Dry gel method 95°C–8 h	10:2:1.35:1000	1.1×10^{-7} (298 K)	0.7×10^{-7} (298 K)	
[7]	α -Al ₂ O ₃ disk	Secondary growth 90°C–2 h, 2 cycles	10:2:5:1000	1.0×10^{-7} (298 K)	1.52×10^{-8} (298 K)	0.53×10^{-8} (298 K)

*Prepared by microwave heating during 15 min.

bar is below the Knudsen values (which are 3.74 for H_2/N_2 and 8.54 for H_2/SF_6), indicating that part of the permeation takes place through spaces larger than the structural pores of the A-type zeolite.

In general, the permselectivity values H_2/N_2 , H_2/SF_6 and the H_2 permeance were found to be higher for stainless steel supports, although for H_2/SF_6 the theoretical Knudsen value selectivity (8.54) was never reached. Temperature programmed permeation experiments (not shown) carried out as described in [13] showed that for membranes prepared on stainless steel tubes all gases displayed a shallow minimum with temperature, at around 373–423 K, except for H_2 , where the minimum was more pronounced. In contrast, for membranes prepared on alumina tubes, a smooth decrease of the N_2 and SF_6 permeation fluxes with temperature was observed. It can be concluded that the contribution of defects was higher for the membranes prepared on alumina, since a Knudsen flow contribution would give a descending flux-temperature curve. On the other hand, the existence of a minimum followed by a marked increase of permeation with temperature indicates a preponderance of activated permeation for the zeolites prepared on stainless steel, and therefore a lower concentration of defects, in

agreement with the separation factors found in this work.

The XRD patterns shown in Fig. 1 for samples MSS2, MSS3, MA1 and MA2 show that zeolite A was obtained on stainless steel supports, while on alumina the characteristic peaks of zeolite A were not observed. Both factors (the XRD patterns and the poorer performance of membranes prepared on alumina) indicate that there is a considerable lower amount of zeolite A synthesised on alumina supports under the conditions given in this work. One possible explanation may be related to the partial dissolution of the support during synthesis, giving rise to a higher Al/Si ratio that would shift the local composition (in the vicinity of the support) towards values less suitable for the formation of zeolite A.

Fig. 2 shows the top surface and cross section of MSS3 sample. The successive deposition of material over the surface may be observed. The first layers seem better crystallised, showing the characteristic zeolite A structure. However, further synthesis leads to poorly connected, amorphous-looking deposits. In the lateral view, a continuous layer with a dense appearance and well attached to the support can be observed. The estimated thickness for the zeolite layer on the MSS3 membrane was approximately 30 μm .

Table 3
Summary of single gas permeances for A-type zeolite membranes before Pd deposition

Membrane code	Temp., K	H_2 permeance ($mol/m^2.s.Pa$)	Ideal H_2/N_2 selectivity	Ideal H_2/SF_6 selectivity
MSS4	323	1.18×10^{-6}	3.98	6.4
	373	6.35×10^{-7}	3.332	6.35
	473	1.00×10^{-6}	3.19	5.84
MA3	323	1.48×10^{-7}	1.63	4.63
	373	1.07×10^{-7}	1.42	3.55
	423	7.27×10^{-8}	1.79	3.39
	473	7.93×10^{-8}	1.41	3.52

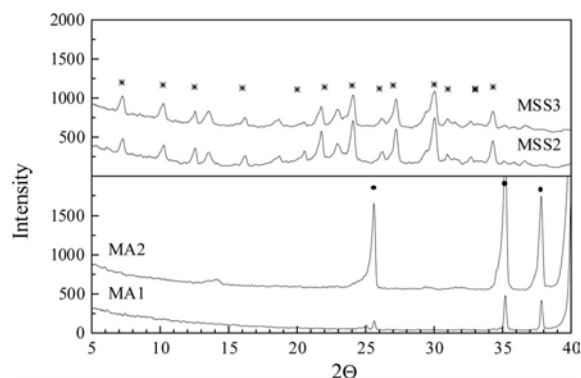


Fig. 1. XRD patterns of membranes MSS2, MSS3, MA1, MA2 (stars for the main reflections of A-type zeolite, circles for the main reflections of α - Al_2O_3 support).

3.2. Permeation tests for Pd composite type-A zeolite membranes

The permeation tests carried out on Pd-modified membranes under a pressure gradient did not show any beneficial effect of Pd incorporation in terms of the separation factors achieved. Both N_2 and H_2 gas permeances increased ($2.65 \times 10^{-7} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$ at 473 K for MSS2 vs. $2.28 \times 10^{-6} \text{ mol/m}^2 \cdot \text{s} \cdot \text{Pa}$ for Pd+MSS2), giving similar permeation trends with temperature, and roughly the same separation factors (≈ 3.6) were observed. However, when the permeation tests were carried out at the same total pressure on both sides of the membrane, using a sweep gas on the permeate side, considerably higher separation factors were found. Thus, an ideal selectivity $\text{H}_2/\text{C}_3\text{H}_8$ of 17.35 was measured for membrane MSS2 at 323 K. Membrane MSS3 gave lower separation factors, but these were above the theoretical Knudsen value (5.75 at 573 K).

The separation performance for binary mixtures was studied for samples MSS2 and MSS3 (see Table 4). Above 373 K, the permeation flux increased with temperature in all cases, indicating a prevalence of the flux through micropores. Membrane MSS2 showed a maximum separation factor of 7.28 at 323 K. For

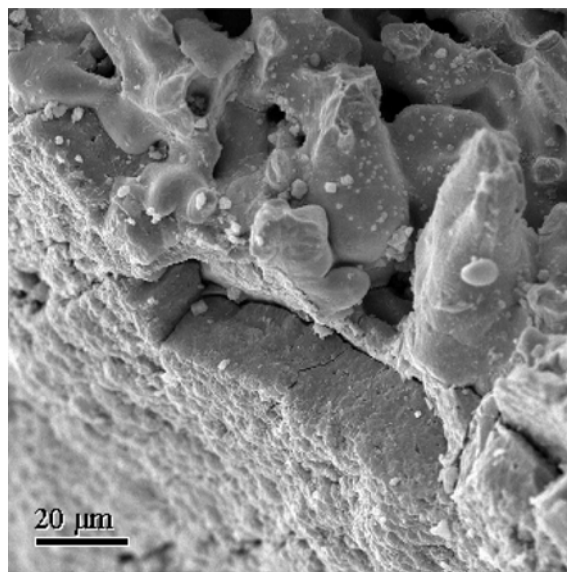
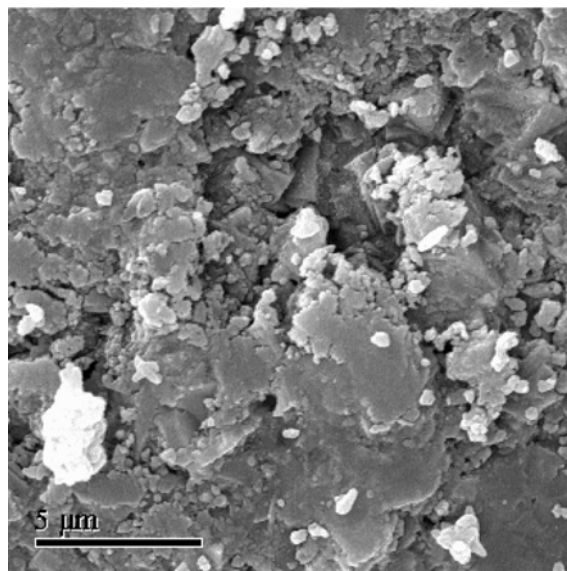


Fig. 2. SEM images of top surface and cross section of membrane MSS3.

H_2/N_2 mixtures, separation factors higher than Knudsen values were also obtained with the MSS3 membrane (e.g., 4.34 at 573 K). It can be concluded that the performance of the A-type zeolite membranes over stainless steel tubes for H_2 separation improved due to Pd deposition, although the improvement was modest since non-

Table 4

Permeation of equimolar H₂/C₃H₈ mixtures through MSS2 and MSS3 membranes (Ar/feed = 50:50)

Sample	Temp., K	H ₂ flux, mol/m ² .s.Pa	C ₃ H ₈ flux, mol/m ² .s.Pa	Separation factor H ₂ /C ₃ H ₈
MSS2	323	4.81×10 ⁻⁷	6.47E-8	7.28
	373	3.44×10 ⁻⁷	6.35E-8	5.72
	523	1.62×10 ⁻⁷	1.90E-7	4.82
MSS3	373	2.06×10 ⁻⁷	4.46×10 ⁻⁸	4.62
	473	2.46×10 ⁻⁷	6.11×10 ⁻⁸	4.02
	573	4.45×10 ⁻⁷	1.02×10 ⁻⁷	4.38

selective inter-crystalline voids still remained in the membrane structure. While the methods used to block the zeolite defects via Pd deposition clearly need development, the ultimate goal of attaining a H₂ permselective structure remains very attractive: a Pd-zeolite composite membrane would contain much less Pd and would be more robust than their dense membrane counterparts with a continuous Pd film.

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