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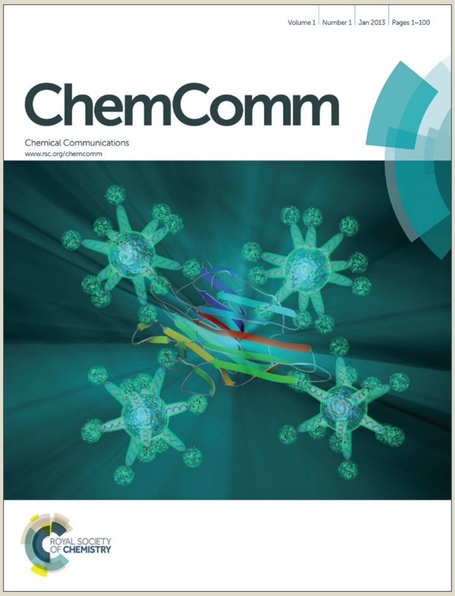

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High selectivity ZIF-93 hollow fiber membranes for gas separation

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Zeolitic imidazolate framework-93 (ZIF-93) continuous membranes were synthetized on the inner side of P84 co-polyimide hollow fiber supports by microfluidics. MOF and polymer showed high compatibility and the membrane exhibited H_2/CH_4 and CO_2/CH_4 separation selectivities of 97 (100 °C) and 17 (35 °C), respectively.

Since their discovery, MOFs (metal-organic frameworks), hybrid crystalline materials developed in recent decades, have been employed to accomplish with the separation requirements of polymeric membranes so as to make them attractive in terms of simultaneous high permeation and selectivity.[1-4] The organic moieties of MOFs allow them to act synergically with polymers ensuring a proper adhesion and bonding, while their narrow microporosity (with tunable pore sizes) helps split the feed components with a high selectivity.[5] The semi-rigid crystalline structures of MOFs enhance their affinity with polymers, avoiding the creation of defects due to thermal expansion, something which typically occurred with inorganic materials (silica or zeolites) when supported on porous inorganic supports.[6-8] In any event, works from Ge et al.[9] and Severance et al.[10] where Al-rich zeolites were grown on polymeric surfaces were reported.

Both MMMs (mixed-matrix membranes) and supported MOF-polymer membranes have been developed for gas separation,[11-13] liquid phase pervaporation[14] and nanofiltration[15] processes. Recently some authors have used hollow fiber (HF) shaped polymers as membrane supports for MOF continuous layers. HKUST-1 and ZIF-90 layers were hydrothermally grown on the outer surface of PAN[16] and Torlon[17] HFs, respectively, while Mao et al. used a pressure-assisted method on PVDF to support HKUST-1.[18] Brown et al. first fabricated an inner-supported ZIF-8 membrane inside Torlon HFs by counter-diffusion growth.[19] Interfacial synthesis was also later applied on PBI-based supports by Biswal et al.[20] At the same time, we developed a method where all the solutions were entirely pumped in the lumen of a polysulfone HF by microfluidics for fabricating ZIF-7 and ZIF-8 permselective membranes for hydrogen separation.[21] These membranes move towards the eco-friendly intensification of the separation processes: small amounts of reactant give rise to shielded MOF HF-supported membranes more suitable for scaling-up.

In the present study, ZIF-93 (Zn(4-methyl-5-imidazolecarboxaldehyde)$_2$), belonging to a subclass of highly stable MOFs called ZIFs (zeolitic imidazolate frameworks), was grown inside co-polyimide P84 HFs (202 ID and 356 OD μm, respectively) using a microfluidic approach developed in our recent previous work (see experimental details in †ESI).[21] ZIF-93 (*rho* structure)[22-24] is for the first time published here as HF continuous membrane. ZIF-93, as well as its isomer SIM-1,[25,26] has become attractive because of its post-functionalization availability.[27,28] The aldehyde functionalization of the imidazolate ligand can be reduced or transformed into an imine with a pendant aliphatic chain which modifies the pore size and the character of the structure.

Due to the lack of access to the interior of the HF for proper characterization, Fig. 1a shows the XRD diffraction of a ZIF-93 dissolved membrane compared with the pattern of the powder collected during the synthesis. With the dissolution of the ZIF-93 membrane the MOF becomes evenly distributed across the composite produced and accessible for characterization purposes. Both dissolved membrane and powder show a correspondence with the simulated *rho* structure of ZIF-93[29] and confirm the MOF presence inside the HF support.

ATR-FTIR analyses (Fig. 1b) show how the ZIF-93 was invisible for infrared radiation in an as-synthesized membrane owing to the P84 polymer surrounding it. When the membrane was dissolved for homogeneous MOF distribution and easier characterization, as explained above, typical peaks for ZIF-93

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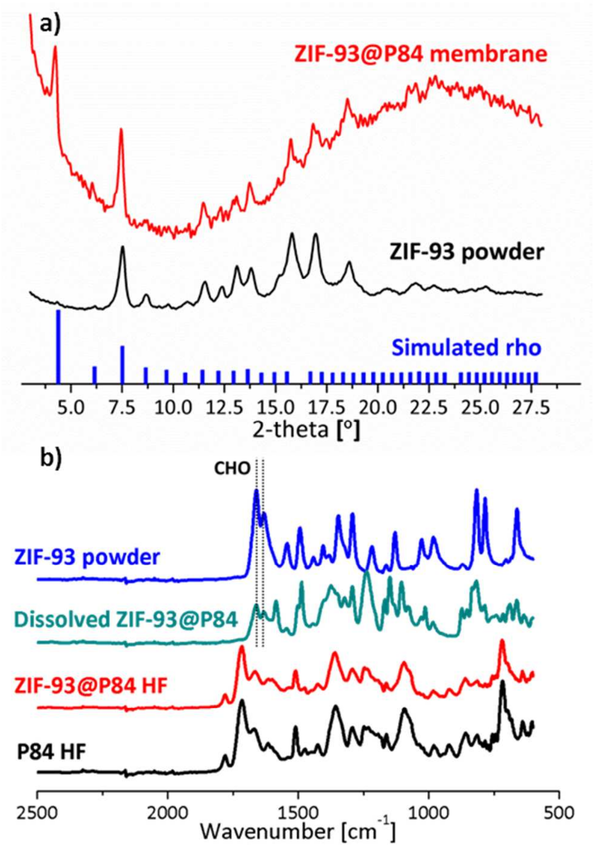

Fig. 1 (a) XRD spectra of a dissolved ZIF-93@P84 membrane compared with the patterns from the powder collected at the exit of the fiber during the membrane fabrication and with the simulated *rho*-structure.[29] (b) ATR-FTIR spectra of dissolved and as-synthesized ZIF-93@P84 membranes compared with the bare P84 HF support and the ZIF-93 powder collected during the corresponding membrane synthesis.

(1633-1658 cm^{-1}, aldehyde group) were observed. This peak is the most intense in the spectrum of the pure powder collected during the membrane synthesis (Fig. 1b).

The inner surface of a ZIF-93@P84 HF membrane was then characterized by SEM. A 2.6 ± 0.4 mm continuous intergrowth MOF layer is shown in Fig. 2a, strongly attached on the inner surface of the P84 HF, with an uninterrupted wide interface between the two materials indicating a strong affinity. The polymer shows a high void fraction with small pores. The enhanced ZIF-93-polymer cohesion was then analyzed by means of a lamella fabricated by Ga-FIB (Fig. 2b). EDX characterization allowed the obtaining of spectra on each zone, which revealed the presence of Zn metal some micrometers (4.1 ± 0.2 mm) deep inside the P84 porosity. This interpenetrated region can be considered as a composite layer with a high loading of MOF in polyimide.

The MOF content inside each fiber was finally evaluated from the residue left by the calcined membranes (considered as ZnO, see Fig. S1 (†ESI)). A high ZIF-93 content as well as a lower degradation temperature (10.6 wt% and 580 °C) were observed for the synthesized membranes compared with the pure polymer (with a maximum oxidation rate at 615 °C). The ZIF-93 MOF particles, shielded inside the HF lumen, degraded first and released Zn metal particles that acted as catalysts in the decomposition of the co-polyimide P84, which became oxidized at a lower temperature.

Owing to their ordered microstructures with narrow pore sizes, ZIFs have been applied to gas separation processes driven by molecular sieving or preferential adsorption mechanisms. ZIF-93 pore size (0.36 nm as predicted by Ray et al.)[23] would be useful in the rejection of large molecules (CH_4, 0.38 nm) while allowing the permeation of smaller H_2 and CO_2 (0.29 and 0.33 nm, respectively) through its porosity. Equimolar H_2/CH_4 and CO_2/CH_4 gas mixtures were fed inside the membrane at 35 and 100 °C (Fig. S2 (†ESI)). The results obtained with the ZIF-93 membranes in the separation tests are shown in Fig. 3.

A H_2 permeance of $3.5 \pm 0.4 \cdot 10^{-9}$ $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ (10.6 GPU) with a H_2/CH_4 selectivity of 59.7 ± 7.4 were obtained at 35 °C. The free diffusion of the H_2 molecules and therefore the separation performance was enhanced at a higher temperature (100 °C), giving rise to a selectivity of 97.2 ± 6.0 with a H_2 permeance of $1.1 \pm 0.1 \cdot 10^{-8}$ $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ (32 GPU). The 8-ring *rho*-ZIF-93 pore window acts as a sieve rejecting the CH_4 molecules at any temperature and leading to high selectivity values. The high selectivities suggest defect-free membranes.

An interesting selectivity was obtained when separating the CO_2/CH_4 mixture at 35 °C (16.9 ± 3.8) with a CO_2 permeance of $7.7 \pm 1.5 \cdot 10^{-10}$ $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$ (2.3 GPU), favored by the CH_4 exclusion. This selectivity value is not far from the simulated value of 26.7 given by Ray et al.,[23] who found that ZIF-93 was the best performing ZIF in this separation of a series including ZIF-25, -71, -93, -96 and -97.

Moreover, the affinity between the crystalline MOF layer and the polymeric support, due to their analogous character, is evidenced in this work. The growing of a continuous ZIF-93 layer on the inner surface of a P84 HF together with the annealing treatment carried out improved the permselective performance of the pure polymer ($1.4 \cdot 10^{-7}$ $mol \cdot m^{-2} \cdot s^{-1} \cdot Pa^{-1}$, 429 GPU, with a H_2/CH_4 selectivity of 4.9). These properties are far from the intrinsic separation of P84: HF fabrication process (see †ESI) did not aimed to prepare selective defect-free membranes but HF supports with an open porous structure not offering a high resistance to gas flow and simultaneously being suitable for MOF growth.

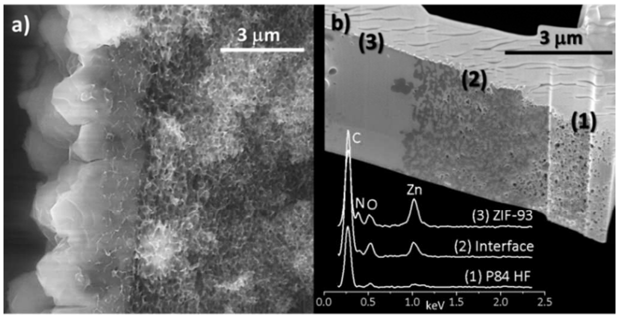

Fig. 2 (a) SEM cross-section image of the MOF-coated inner surface of an as-synthesized ZIF-93@P84 membrane; (b) a lamella made with Ga-FIB etching and

EDX spectra measured in the MOF layer, support and interface, showing the MOF attachment to the polymer.

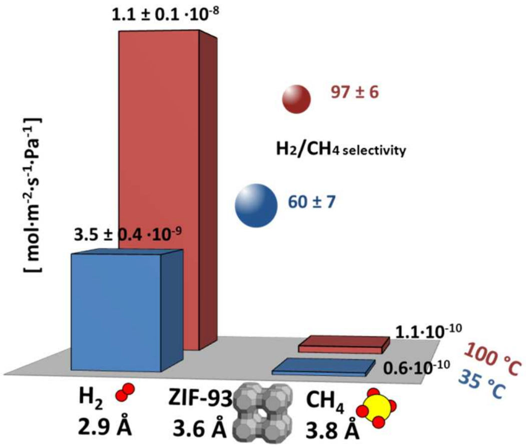

Fig. 3 Averaged performance values of two ZIF-93@P84 HF membranes in H_2/CH_4 mixture separation at 35 and 100 °C. Dots represent the mixture selectivities, whereas bars are permeances.

In summary, a ZIF-93 continuous membrane was for the first time fabricated and applied on the separation of gas mixtures driven by molecular sieving mechanisms: high selectivities in the H_2/CH_4 (59.7) and CO_2/CH_4 (16.9) mixtures at 35 °C were obtained. In addition, a P84 co-polyimide HF was used as support in the microfluidic membrane syntheses, comprising an ecofriendly intensification of processes owing to the high area to volume ratio exhibited and the reagent saving achieved,[21] making them suitable for scaling up. The organic moieties of the ZIF-93 and the polymer ensured their affinity and compatibility, preventing from any damage when operating at high temperature conditions (H_2/CH_4 selectivity of 97.2 at 100 °C). Compared to previously reported MOF membranes on HFs,[17-20] the inner-shielded membranes synthetized in this work showed higher selectivities with intermediate permeances, representing a well-balanced performance. A more permeable HF support could be used to reduce the flow resistance and then increase the permeation performance of the membrane.

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