

## Electronic supplementary information

### Selective blocking of grain boundary defects in high-flux zeolite membranes by coking

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#### Membrane synthesis

Supported zeolite membranes comprised of an H-ZSM-5 film with a thickness of *ca.* 300 nm and a Si/Al ratio of 139<sup>1</sup> were prepared as described in detail in our earlier work<sup>2</sup>. A porous graded  $\alpha$ -alumina disc (Fraunhofer IKTS, Germany) was used as the support. Prior to the film synthesis, the supports were masked as described elsewhere<sup>3</sup> and then seeded with colloidal MFI crystals of 50 nm in diameter. The film synthesis was carried out for 36 h at 100°C in a solution with a molar composition of 3TPAOH : 25SiO<sub>2</sub> : 1450H<sub>2</sub>O : 100C<sub>2</sub>H<sub>5</sub>OH. After the synthesis, the membranes were rinsed with a 0.1 M ammonia solution for 24 h and then calcined for 6 h at 500°C at a heating rate of 0.2°C min<sup>-1</sup> and a cooling rate of 0.3°C min<sup>-1</sup>.

#### Membrane characterisation

##### *Scanning electron microscopy characterisation*

Scanning electron microscopy (SEM) characterisation of the membranes was carried out using a Magellan 400 (the FEI Company, Eindhoven, the Netherlands) SEM instrument without coating the samples. Cross-sections of the membranes were obtained by fracturing the samples with a pair of cutting pliers.

##### *Permporometry characterisation*

In order to estimate the amount and size of the defects, the membranes were characterised by *n*-hexane/helium permporometry<sup>4</sup> as described in detail in our earlier work<sup>5</sup> and in brief here. The membranes were sealed in a stainless steel cell using graphite gaskets (Eriks, the Netherlands). In order to remove any adsorbed compounds, the membranes were heated to 300°C at a heating rate of 1°C min<sup>-1</sup> and kept at this temperature for 6 h in a flow of pure helium. Permporometry tests were carried out at 50°C and a total pressure difference across the membrane of 1 bar with the permeate stream kept at atmospheric pressure. The relative pressure of *n*-hexane was raised in a step-wise manner from 0 to *ca.* 0.4. At each relative pressure, the system was allowed to achieve steady-state. For removing *n*-hexane from the permeate stream, a condenser kept at -40°C followed by a column packed with activated carbon was used. The permeate volumetric flow rate was measured with a soap bubble flow meter. A detailed procedure for estimation of the relative areas of defects from permporometry data is given in our earlier work<sup>5</sup>. In brief, the defect width was calculated from *n*-hexane relative pressure using either the Horvath–Kavazoe equation (micropore-range defects) or the Kelvin equation (mesopore-range defects) adjusted for the adsorbed layer thickness by the Harkins-Jura equation. For each defect interval, the average defect width was then calculated. Based on the average defect width, the average helium diffusivity in each defect interval was estimated using the gas-translational model. Knowing the diffusivity, the helium molar flux was further calculated from Fick's law. Finally, the defect area was estimated as the ratio between helium molar flow and flux through the defects in that particular interval. The experimental flux of permeating component *i*,  $J_i$  (mol s<sup>-1</sup> m<sup>-2</sup>), was estimated from the measured molar flow of the corresponding component through the membrane,  $F_i$  (mol s<sup>-1</sup>) as

$$J_i = F_i/A, \text{ where } A \text{ is the membrane area (m}^2\text{).}$$

The experimental permeance of component  $i$ ,  $\Pi_i$  ( $\text{mol s}^{-1} \text{ m}^{-2} \text{ Pa}^{-1}$ ), was calculated from the flux of the corresponding component through the membrane as

$\Pi_i = J_i / \Delta P_i$ , where  $\Delta P_i$  (Pa) is the partial pressure difference of component  $i$  across the membrane.

### Coking procedure

After the permoporometry characterisation, the  $n$ -hexane was removed from the membrane by flushing with pure helium at 50°C overnight followed by calcination in air at 350°C for 15 h. Thereafter, the feed was changed to a helium flow saturated with *iso*-propanol at 20°C (the temperature of the saturator was maintained by a thermostat). The feed and permeate pressures were atmospheric. Pure helium was used as a sweep gas on the permeate side. The membrane temperature was kept constant at 350°C for the treatment. The duration of the treatment was varied between 1 and 25 hours to study the effect of treatment (coking) time. After each treatment, the membrane was flushed with pure helium overnight and cooled to 50°C.

### Separation experiments

After completion of the permoporometry experiment, the feed was changed to an equimolar mixture of  $n$ -hexane (Alfa Aesar, 99%) and 1,3,5-trimethylbenzene (TMB, Sigma-Aldrich,  $\geq 99.0\%$ ) in a flow of helium. The feed pressure as well as the permeate pressure were kept at atmospheric pressure. The membrane coked for 25 h was first equilibrated with the feed at 50°C overnight. The next day, separation experiments were carried out using helium as sweep gas at a temperature of about 160°C. The permeate composition was analysed with a GC (Varian chrompack CP-3800) connected on-line.

The  $n$ -hexane/TMB separation factor was estimated as

$\beta_{\text{Hex/TMB}} = \frac{y_{\text{Hex}} / y_{\text{TMB}}}{x_{\text{Hex}} / x_{\text{TMB}}}$ , where  $x$  and  $y$  are the molar fractions in the feed and permeate, respectively.

### References

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