Incorporation of nano-sized zeolites in membranes

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The first incorporation of nano-sized zeolites in membranes is reported and polydimethylsiloxane membranes filled with colloidal silicalite-1 are applied in the pervaporation of ethanol–water mixtures.

The incorporation of zeolites and porous amorphous fillers in dense membranes improves the performance (normalized flux and selectivity) of these membranes in both gas separation and pervaporation for several types of feed mixtures.[1–4] All porous fillers reported up to now have particle sizes in the micron range. As a consequence, the minimal membrane thickness of the composite membranes was inherently higher than that of most unfilled membranes and the absolute fluxes remained low. The recent development of small ‘nano-sized’ colloidal zeolites leads to the possibility for the preparation of thin, defect-free, filled polymer layers. The synthesis of stable silicalite-1 particles with diameters as small as 70 nm was reported, as well as that of zeolite A (in the range 50–230 nm) and zeolite Y (80–110 nm).[5–7] We report here, the first incorporation of nano-sized zeolite particles in a polymeric membrane, that of silicalite-1 in PDMS (polydimethylsiloxane), and the performance of these membranes in the pervaporation of an aqueous ethanol solution.

Nano-sized silicalite-1 was synthesized following a procedure reported earlier:[8] tetraethylorthosilicate (98%, Acros Chimica), tetrapropylammonium hydroxide (TPAOH, 40% aqueous solution, Alfa) and water were mixed in order to obtain a mixture with a molecular composition of 9 TPAOH : 24.5 SiO_2 : 416 H_2O. The mixture was stirred for 24 h at room temperature and refluxed for 3 days at 100 °C. The silicalite-1 crystals were separated from the mother liquor by repeated centrifugation and washing. After redispersion and freeze-drying, the powder was calcined in air (1 °C min^{-1} heating rate, 2 h at 110 °C and 12 h at 550 °C). The particle size and shape observed by SEM (Fig. 1) and XRD were in good agreement with previous results.[8] The dry zeolite was dispersed in toluene by stirring and ultrasonic treatment. The suspension was then mixed with PDMS (prepolymer and crosslinker in a 10 : 1 ratio, General Electric, RTV 615 A and B) so as to give a 15 vol% solution of membrane constituents (polymer + zeolite) with the desired polymer : zeolite ratio. After a prepolymerisation step at 70 °C for 45 min, the casting solution was poured into a Petri dish and the solvent was evaporated overnight. To obtain complete crosslinking, the membrane was placed in a vacuum oven at 100 °C for 2 h. The maximum silicalite-1 load leading to a macroscopically homogeneous membrane was 30 wt%.

Dispersion of the zeolite in the polymer matrix was investigated by SEM. Fig. 2 shows the cross-section of a PDMS membrane containing 30 wt% nano-sized silicalite-1. Whereas a homogeneous dispersion of large zeolite crystals throughout a polymer matrix has not been reported to be problematic,[1–4] the distribution of the 70 nm crystals in the membrane was not homogeneous. An attempt was made to increase the zeolite loading and the dispersion by improving the contact between the polar zeolite surface and the apolar polymer. The nano-sized silicalite-1 was treated with a silane coupling agent to cover the surface with hydrophobic trimethylsilyl groups. The dry zeolite was dispersed in toluene and *N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide (MSTFA, Acros Chimica, 97%) was added in a five-fold excess, with respect to the amount of silanols present. This number was estimated based on the external surface area of silicalite (45 m^2 g^{-1})[8] and assuming a silanol density of 6 OH nm^{-2}. After ultrasonic treatment, the mixture was stirred at room temperature and refluxed overnight. Removal of unreacted MSTFA was achieved by redispersion in toluene and centrifugation (30 min at 22 100 *g*). The silicalite-1 was finally recovered by evaporating the toluene. Silylation had a positive effect on the maximum amount of zeolite that could be incorporated in the polymer matrix from *ca.* 30 wt% for the non-silylated zeolite up to 40 wt% for the silylated sample. SEM observations of cross-sections of membranes, however, did not reveal an improved dispersion.

The synthesized membranes were evaluated in the pervaporation of a 6 wt% aqueous ethanol solution at three different temperatures. The vacuum at the permeate side was maintained at a pressure below 2 mbar and the permeate was trapped with liquid nitrogen. All reported membranes had thicknesses between 200 and 400 μm. The fluxes were normalized to a thickness of 100 μm assuming an inverse proportionality

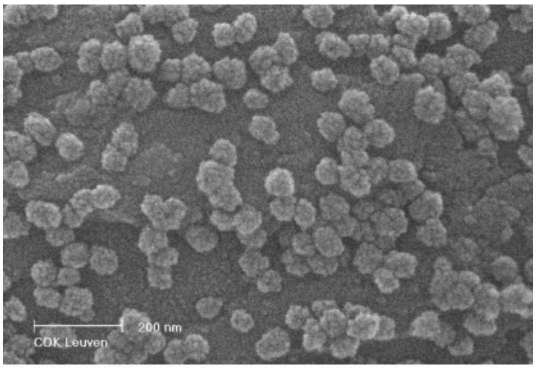

Fig. 1 SEM image of nano-sized silicalite.

Fig. 2 Cross-section of a PDMS membrane filled with 30 wt% nano-sized silicalite.

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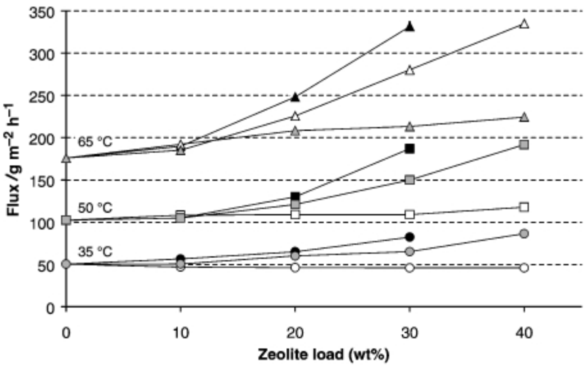

Fig. 3 Total fluxes, normalized to a membrane thickness of 100 μm, at three different temperatures for composite membranes prepared with micron-sized zeolites (open symbols) and nano-sized zeolites: silylated (grey symbols); non-silylated = black symbols).

between the flux and the membrane thickness. Selectivity is expressed as $\alpha = (y_a/y_b)/(x_a/x_b)$ in which y refers to the concentration of the components in the permeate and x to the concentration in the feed. Permeates were analysed by adding methanol as a standard and acetone as a homogenising solvent, followed by analysis with GC. Fig. 3 and Table 1 show the total normalized pervaporation flux and selectivity, respectively. At three different temperatures, a comparison was made between the performance of composite membranes filled with the self-prepared nano-sized silicalite and membranes filled with a commercial micron-sized silicalite (CBV-2802, PQ zeolites, Si:Al ratio = 550:1, 0.4–0.8 μm). The nano-sized zeolites show much improved pervaporation results compared with the micron-sized silicate membranes: both flux and selectivity are drastically increased at the highest loadings. Best results were obtained with the PDMS membrane containing 40 wt% of silylated nano-sized silicalite-1.

An explanation for this remarkable effect of nano-sized zeolites in PDMS for the pervaporation of ethanol–water mixtures, is probably related to the mesopores reported to be present in the silicalite-1 samples.[8] These mesopores most probably arise due to voids between the nanocrystals. The extent to which these mesopores and their silylation is responsible for the beneficial effect of the nano-sized zeolites in the pervaporation process, possibly acting as freeways for the preferentially sorbed ethanol, is currently being investigated.

Table 1 Selectivities obtained at different temperatures for composite membranes filled with micron- or nano-sized zeolties

T/°C	Filler load (wt%)	Micron-sized	Nano-sized	Nano-sized (silylated)
35	0	9.0	9.0	9.0
	10	8.8	10.1	9.8
	20	8.6	11.4	12.1
	30	8.9	15.7	13.9
	40	9.2		16.4
50	0	8.6	8.6	8.6
	10	9.2	9.9	9.7
	20	11.3	11.9	10.9
	30	11.5	15.3	12.3
	40	11.8		15.7
65	0	8.7	8.7	8.7
	10	8.9	10.5	9.5
	20	10.6	12.5	10.8
	30	11.7	14.3	11.9
	40	11.9		14.6

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