A new titanosilicate umbite membrane for the separation of H_2

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A new microporous titanosilicate umbite membrane has been synthesized on commercial porous TiO_2 tubular supports. This membrane is able to separate H_2/N_2 mixtures (with selectivities as high as 48) even in the presence of water.

The separation of H_2 from its mixtures with gases and water through inorganic membranes is still a matter of considerably effort.[1] An affordable, H_2-permselective membrane could be a definitive advantage in the implementation of challenging processes, among them purification of hydrogen-containing streams and H_2 proton-exchange membrane (PEM) fuel cells.[2] However, in most membrane-separation processes water has a negative influence on membrane performance.[3] Research in recent years has produced zeolitic membranes that can selectively separate water from its mixtures with permanent gases. In this case, due to the preferential adsorption and/or capillary condensation water permeates selectively,[4] and as a consequence the gas permeance is strongly decreased. Here the microporous titanosilicate ($K_2TiSi_3O_9 \cdot H_2O$)[5–7] with the structure of umbite[8] has been reproducibly prepared for the first time as a continuous, *ca.* 5 μm thick membrane on porous TiO_2 tubular asymmetric supports by seeded hydrothermal synthesis, a similar strategy to that previously used to synthesise titanosilicate ETS-4[9] and ETS-10[10] membranes. Umbite is a most interesting material to be prepared as a membrane since, due to its very small pore size (around 0.3 nm), it does not adsorb N_2[5] and displays a very slow diffusion of water,[11] even though it can be reversibly dehydrated.

Ti-umbite membranes were prepared on porous TiO_2 asymmetric tubular supports (Inocermic) with 5 nm pore diameter. The macroporous part of the support is made of α-alumina, while the internal and external diameters of the tubes were *ca.* 7 and 10 mm, respectively, and they were 8 cm long (5 cm permeable). The membranes were prepared using the following gel molar composition: 5.3 K_2O:3.6 SiO_2:TiO_2:120 H_2O. The precursor reactants were $TiCl_3$ solution (15 wt% $TiCl_3$, 10 wt% HCl, Merck), deionized H_2O, KCl (99 wt%, Merck), KOH (85 wt%, Merck) and fumed silica (Aerosil 300). To prepare 40.7 g of the precursor gel, 2.81 g of Aerosil 300 were dissolved in a solution of 16.4 g of KOH in 16.9 mL of water. To this solution 2.27 g of KCl were added. Then, this solution was mixed with 12.34 g of the $TiCl_3$ precursor, yielding a dark purple gel which was kept under vigorous stirring for 30 min. To oxidize Ti^{3+} to Ti^{4+}, H_2O_2 (30 wt%) was added drop wise until the gel became white. The membranes were prepared by subjecting the seeded substrate to a secondary growth step. For this purpose the tubes, having their external surface wrapped with Teflon tape (also during the hydrothermal synthesis explained below), were immersed once in a water suspension containing 5 wt% Sn-umbite crystals. Because the particle size of Ti-umbite powder is *ca.* 10 μm, a Sn-umbite powder was used as seed as a means of obtaining an optimum seeded layer for the secondary growth. This powder was previously prepared with an average particle size of *ca.* 300 nm (measured by photon correlation spectroscopy, PCS, Malvern Zetasizer 3000 HS).[12] After drying at 120 °C, the seeded supports (using a 5 wt% suspension in an ultrasound bath for 15 minutes) were placed either vertically or rotating horizontally in a Teflon-lined autoclave into which the synthesis mixture was poured. The hydrothermal synthesis was carried out at 230 °C for 48 hours. The synthesis was finished by quenching the autoclave in running water. The membranes were washed with water by means of a washer flask for 1 minute, dried overnight at 100 °C and, once cooled, washed again with 80 mL of acetone (for 8 minutes) after 1 minute ultrasonication.

The umbite membranes were characterized by scanning electron microscopy (SEM, JEOL JSM-6400) and X-ray diffraction (XRD, Philips X'pert MPD diffractometer using CuKα radiation). The membranes, previously pre-treated in Ar flow at 170 °C for 10 hours, were also tested for the separation of a H_2/N_2 mixture. The membrane to be tested was placed in a stainless steel module and sealed with silicone o-rings. The module was heated in an electrical oven. A 70/70 cm^3 (STP) per min H_2/N_2 mass-flow controlled (Bronkhorst Hi-Tec, F-201C-FA-22-V) stream was fed into the tube side (retentate), while the permeating side (shell side) was swept with 135 cm^3 (STP) per min of Ar. The pressure difference across the membrane was zero. The exit streams from the retentate and permeate sides were analyzed by on-line mass spectrometer (OmniStar™, Pfeiffer Vacuum QMS 200). The separation selectivity was calculated as the ratio of permeances, using the log-mean partial pressure difference to obtain permeances. Mass balance closures for the different species based on the composition and flow rate of the feed and the two exit streams were better than 5%.

Fig. 1a shows the XRD pattern of a Ti-umbite membrane prepared under the same conditions as membrane M1 (Table 1). The comparison of M1 signals with the Ti-umbite powder reflections in Fig. 1b reveals that pure umbite was obtained with preferential orientation. Membranes M2 and M3 prepared under rotation gave rise to a kind of preferential orientation that diminishes the main umbite peaks producing XRD patterns (not shown) where the signals coming from the support are very strong.

The 5 nm TiO_2 asymmetric tubular supports employed for the umbite synthesis provide a smooth surface that favours the growth of a continuous layer of well intergrown crystals, as shown in Fig. 2a. The cross section of the membrane reveals (Fig. 2b) the presence of a continuous umbite membrane of thickness around

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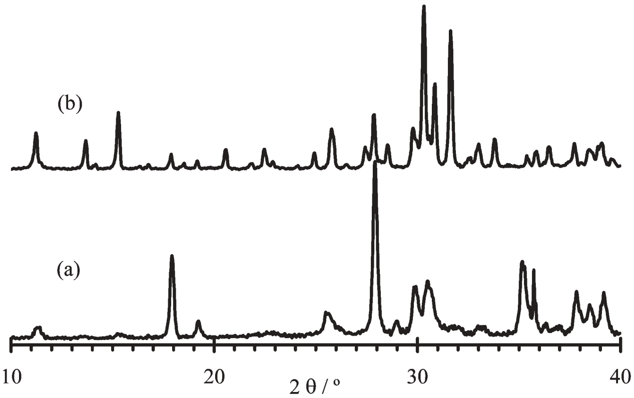

Fig. 1 XRD patterns of: (a) Ti-umbite membrane, (b) Ti-umbite powder.

Table 1 Ti-umbite membranes. Permeances of the equimolar mixture at 60 °C

Membrane	Autoclave position	Washing	H_2 permeance/mol $(m^2\ s\ Pa)^{-1}$	H_2/N_2 selectivity
M1	Vertical	Water[a]	4.6×10^{-8}	48
M2	Rotating	Acetone	14×10^{-8}	36
M3	Rotating	Acetone	4.4×10^{-8}	40

[a] Flushed with water for 1 minute.

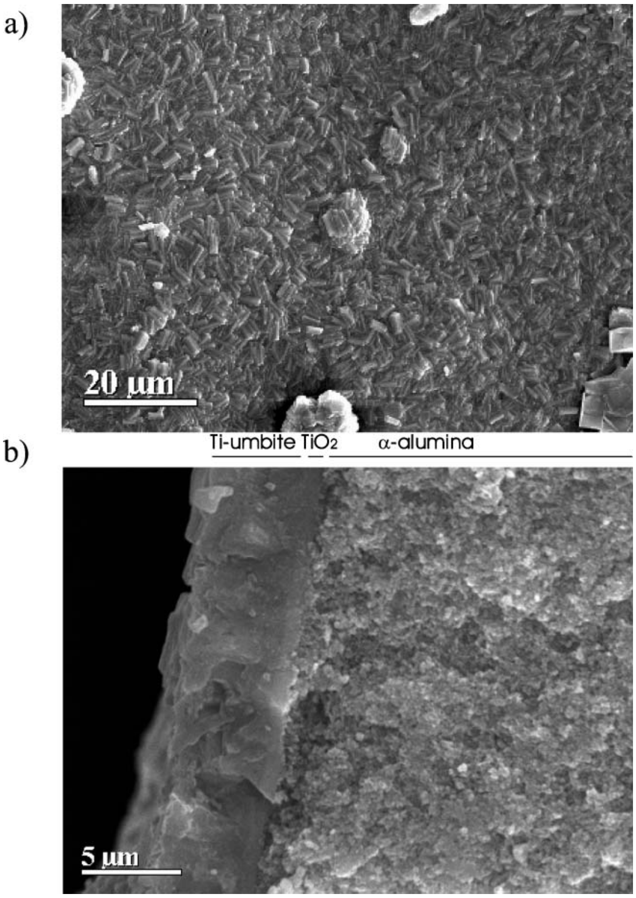

Fig. 2 SEM images of a Ti-umbite membrane: (a) top view, (b) cross section.

5 µm, on top of the very thin, *ca.* 2 µm, TiO_2 layer. Also, the chemical composition of the support, TiO_2, promotes a more homogeneous nucleation and growth of the umbite crystals as membrane.

Table 1 shows the H_2/N_2 separation selectivities obtained at 60 °C for three Ti-umbite membranes. The umbite structure does not adsorb N_2[5] and the adsorption of water occurs very slowly on this material,[11] as a consequence the pore size of the umbite structure should be very small, which justifies, given that H_2 and N_2 kinetic diameters are 0.289 and 0.364 nm, respectively, the high H_2/N_2 separation selectivity, in the 36–48 range, exhibited by our umbite membranes. Also, the separation performance of membrane M1 was tested in the presence of water. Then, when water vapour (1.2% in volume) was added at 60 °C to the H_2/N_2 mixture, the H_2 permeance was only slightly decreased, while the H_2/N_2 separation factor increased by an order of magnitude to more than 200; at 150 °C the separation factor was still 113. The H_2 permeance was in the 3–11 $\times$ 10^{-8} mol $(m^2\ s\ Pa)^{-1}$ interval for all the range of conditions tested. These results seem to indicate that, *unlike other microporous membranes*,[4] water does not permeate through umbite pores but it is capillarily condensed in the defects existing in the membrane. The size and number of these defects should be very limited, since the selectivity of the membrane without water is high. Finally, the stability of membrane M1 was tested for more than 900 hours of operation, involving several heating and cooling cycles.

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