Articles

Synthesis, Characterization, and Separation Properties of Sn− and Ti−Silicate Umbite Membranes

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Microporous stannosilicate ($K_2SnSi_3O_9 \cdot H_2O$) and titanosilicate ($K_2TiSi_3O_9 \cdot H_2O$) with an umbite structure have been prepared as continuous membranes in about 5 μm thick layers on porous α-alumina and TiO_2 tubular supports by seeded hydrothermal synthesis. These membranes are able to separate H_2 from N_2, CO_2, and propane with good selectivity. Some stability problems appeared probably related to the reversible dehydration of the membranes.

Introduction

Since the early 1990s there has been an increasing interest in the synthesis of new ordered microporous materials[1,2] such as titanosilicates[3] ETS-10 and ETS-4 and other heteropolyhedral structures, mesoporous templated silicates, namely M41S,[4] and metal−organic frameworks.[5] This research effort has yielded numerous new materials whose potential applications remain unexplored.[6] In the field of membranes and membrane reactors in particular, only a few such materials have been studied. For instance, membranes with interesting separation properties have been reported for the following zeolite-type materials:[7,8] silicalite, ZSM-5, mordenite, zeolite A, zeolite Y, zeolite beta, ETS-4, ETS-10, and MCM-48. To broaden the scope of application of microporous membranes in separations, membrane reactors and sensors, it is necessary to investigate the preparation of novel zeo-type membranes.

One microporous silicate system attractive for membrane applications is based on the mineral umbite, $K_2(Zr_{0.8}Ti_{0.2})Si_3O_9 \cdot H_2O$, found in the Khibiny alkaline massif (Russia) and described only two decades ago.[9] Umbite-type synthetic materials have been reported recently: $K_2ZrSi_3O_9 \cdot H_2O$,[10,11] $K_2TiSi_3O_9 \cdot H_2O$,[12−14] $K_2SnSi_3O_9 \cdot H_2O$,[15] and $K_2ZrGe_3O_9 \cdot H_2O$.[16] Like the titanosilicates ETS-10 and ETS-4, umbite-type compounds possess framework structures built of MO_6 (M = Zr, Sn, Ti) octahedra and SiO_4 (or GeO_4) tetrahedra. These materials are good cation exchangers, and the ion-exchanged forms of Na^+ and Cs^+−Zr-umbite,[11] NH_4^+, Li^+, Na^+, K^+, Rb^+, and Cs^+−Ti-umbite,[12] and Cs^+ and Sr^{2+} −Sn-umbite[17] have been investigated in detail. Because the one-dimensional eight-membered ring channel (ca. 5.5 × 2.7 Å) is occupied by K^+ and water molecules, Ti-umbite does not adsorb N_2, while the maximum water uptake is 0.082 g/g.[13] Moreover, thermogravimetry reveals a loss of 11 wt % between 35 and 300 °C for Zr-umbite.[11] Although a type I isotherm is expected for such a material, this has not yet been reported. Finally, the temperature of collapse of the structure, at least for Ti-umbite,[12] depends on the cation form, ranging from 100 (NH_4^+) to 600 °C (K^+).

The small pore size of umbite materials grants them potential for separation of H_2 containing mixtures. After a brief communication of the synthesis of the first titanosilicate umbite membrane,[18] here we present in detail the preparation and characterization of umbite-type stannosilicate and titanosilicate membranes on porous α-alumina and TiO_2 tubes

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and their separation properties. The few studies available on membranes of microporous materials related with umbite report on ETS-4[19−21] and ETS-10.[22,23]

Experimental Section

Titanium and tin umbite membranes were prepared on tubular porous α-alumina (symmetric) and TiO_2 (asymmetric) supports (Inocermic) with 1900 and 5 nm pore diameters, respectively. In the case of the TiO_2 supports, the separation layer is on the inner surface of the tubes, α-alumina being the macroporous part of the support. The internal and external diameters of the tubes were about 7 and 10 mm, respectively, and they were 8 cm long (5 cm permeable).

The membranes were prepared using the following gel molar composition: 5.5:3.0:1:120 $K_2O/SiO_2/SnO_2/H_2O$ or 5.3:3.6:1:120 $K_2O/SiO_2/TiO_2/H_2O$. The precursor reactants were $TiCl_3$ solution (15 wt % $TiCl_3$, 10 wt % HCl, Merck), $SnCl_4{\cdot}5H_2O$ (98 wt %, Riedel-de Häen), deionized H_2O, KCl (99 wt %, Merck), KOH (85 wt %, Merck), and fumed silica (Aerosil 300). To prepare 40.8 g of the Sn containing gel, 0.75 g of Aerosil 300 were added to a solution of 1.6 g of KOH in 15 mL of water. After 30 min of stirring a clear solution was obtained. Then, 1.36 g of KCl were dissolved in this first solution. A second solution of 1.39 g of $SnCl_4{\cdot}5H_2O$ in 15 mL of water was continuously stirred for 20 min before mixing with the first solution. A white solution was obtained and vigorously stirred for another 30 min before the final 5.7 mL of water was added. A total of 40.7 g of the Ti containing gel were prepared as follows: 2.81 g of Aerosil 300 were dissolved in a solution of 6.4 g of KOH in 16.9 mL of water. To this solution was added 2.27 g of KCl. This solution was then mixed with 12.34 of the $TiCl_3$ precursor, yielding a dark purple gel which was vigorously stirred for 30 min. To oxidize Ti^{3+} to Ti^{4+}, H_2O_2 (30 wt %) was added dropwise until the gel became white.

The membranes were prepared by subjecting the seeded substrate to a secondary growth step. When symmetric α-alumina supports were employed, the seeding was carried out by rubbing on the outer surface (where the synthesis occurs). In this case, the support was gloved in a finger of latex, and about 120 mg of seeds was placed in the space between the latex and the support. The latex finger was then knotted, and the rubbing was carried out on the external surface of the support. This procedure prevents the loss of small particles coming from the attrition of the seeds. For inner-surface seeding, the TiO_2 asymmetric tubes were immersed once in a water suspension containing 5 wt % umbite powder (the outer surface of the tubes was wrapped with Teflon tape during seeding and the hydrothermal synthesis). The suspension and the porous tubes were placed in a sonication bath for 15 min. This seeding procedure was also employed on the outer surface of some α-alumina supports pretreated with PDDA (poly(diallyldimethylammonium chloride)) polymer.

Because the particle size of the Ti-umbite crystals is about 10 μm, Sn-umbite powders were used as seeds in Sn- and Ti-umbite membranes. Sn-umbite crystals, 0.8−0.9 μm in size, were prepared using the same gel and conditions used for the synthesis of Sn-umbite membranes. These crystals were ground to about 0.7 μm in an agatha mortar and used as seeds for the rubbing and ultrasonic seeding of the α-alumina supports pretreated with PDDA. For the ultrasonic seeding of the TiO_2 supports, Sn-umbite powder was previously prepared with an average particle size of about 300 nm (measured by photon correlation spectroscopy with a Malvern Zetasizer 3000 HS).[24]

Table 1. Some Relevant Data of Sn-Umbite Membranes[a]

membrane	support	autoclave position	H_2 permeance $\times 10^8$ [mol/(m²·s·Pa)]	H_2/N_2 selectivity
SnM1[b]	α−1900 nm	horizontal	2.0	8.1
SnM2	α−1900 nm	vertical	2.3	36
SnM3	α−1900 nm	vertical	0.92	5.1
SnM4	α−1900 nm	vertical	0.92	13

[a] The permeances are given at 60 °C. [b] For this membrane the H_2O/SnO_2 molar ratio in the synthesis gel was 490.

After drying at 120 °C, the seeded supports were placed vertically, horizontally, or rotating horizontally (30 rpm) in a Teflon-lined autoclave where the synthesis mixture was poured. The hydrothermal synthesis was carried out at 230 °C for Ti-umbite and 200 °C for Sn-umbite under autogenous pressure for 48 h. Autoclaves with different volumes were employed so that different amounts of precursor gel were used in the hydrothermal synthesis: 35, 70, and 125 mL, approximately, accounting for about 90% of the volume of the autoclave. The synthesis was terminated by quenching the autoclave in running water. The membranes were washed at room temperature, first with a washer flask for 1 min, and second with 80 mL of distilled water (for 1 h) after sonication for 1 min. They were then dried overnight at 100 °C. Sometimes the membranes were washed with water for only 1 min by means of a washer flask and sonicated in water for 10 s, dried overnight at 100 °C, and once cooled, washed with 80 mL of acetone (for 8 min) after sonication for 1 min.

The umbite membranes were characterized by scanning electron microscopy (SEM) and X-ray mapping (JEOL JSM-6400) and X-ray diffraction (XRD, Philips X′pert MPD diffractometer using Cu Kα radiation). Membranes, previously pretreated in Ar flow at 170 °C for 12−14 h, were also tested for the separation of gas mixtures containing H_2. 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. The 165:70:70 cm^3 (STP)/min $Ar/H_2/N_2$ and $Ar/H_2/CO_2$ and 86:35:35 cm^3 (STP)/min Ar/H_2/propane mass-flow controlled (Bronkhorst Hi-Tec, F-201C−FA-22-V) streams were fed into the membrane side (where the umbite layer was synthesized). The permeate side was flushed with Ar as the sweep gas to create the necessary driving force: 135 and 80 cm^3 (STP)/min for N_2 and CO_2 and propane containing mixtures, respectively. ΔP across the membrane was usually zero. The exit streams from the retentate and permeate sides were analyzed by an on-line mass spectrometer (OmniStar, Pfeiffer Vacuum QMS 200). Ar was used to improve the mass spectrometer performance and also because N_2 was a compound to be analyzed. The separation selectivities quoted below were calculated as permeance ratios, using the log-mean partial pressure difference to obtain the 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%.

Results and Discussion

Preparation of Umbite Membranes. Tables 1 and 2 show some relevant data of, respectively, the Sn- and Ti-umbite membranes. In both cases, the level of H_2 permeance is low

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Table 2. Some Relevant Data of Ti-Umbite Membranes[a]

membrane	support	seeding	autoclave position	washing	H_2 permeance $\times 10^8$ [mol/(m^2·s·Pa)]	H_2/N_2 selectivity
TiM1[b]	α−1900 nm	rubbing	vertical	water	19[c]	11[c]
TiM2	α−1900 nm	rubbing	vertical	water	3.5	8.1
TiM3[d]	α−1900 nm	rubbing	vertical	water	2.6	14
TiM4[e]	α−1900 nm	rubbing	vertical	water	2.7	19
TiM5[f]	α−1900 nm	rubbing	horizontal	water	2.7	8.9
TiM6	α−1900 nm	sonication[g]	vertical	water	12	8.6
TiM7	α−1900 nm	sonication[g]	vertical	acetone	66	19
TiM8	TiO_2 5 nm	sonication	vertical	water[h]	4.8	48
TiM9	TiO_2 5 nm	sonication	rotating	acetone	1.9	30
TiM10	TiO_2 5 nm	sonication	rotating	acetone	4.4	40
TiM11	TiO_2 5 nm	sonication	rotating	acetone	14	36

[a] The permeances are given at 60 °C. [b] The membrane was synthesized at 200 °C for 60 h. [c] At 160 °C. [d,e] Larger autoclaves were used containing 75 and 140 mL of gel, respectively. [f] TiO_2 as the Ti source. [g] The support was pretreated with PDDA. [h] Flushed with water for only 1 min.

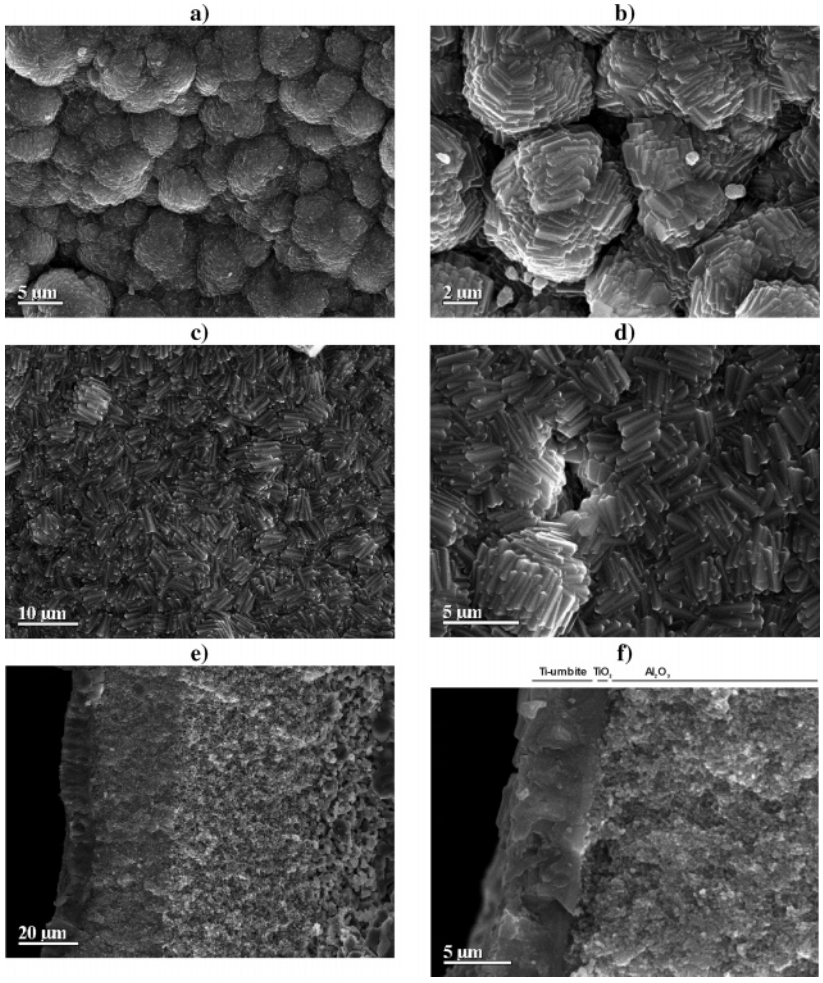

Figure 1. SEM images of Ti-umbite membranes washed with water: (a, b) top views of a membrane prepared on a symmetric α-alumina support; (c, d) top views of a membrane prepared on a TiO_2 asymmetric support; and (e, f) cross sections of the membrane depicted in parts c and d.

by comparison, for instance, with MFI-type membranes with permeances for this gas larger than 10^{-6} mol/(m^2·s·Pa).[25] This may be ascribed to the small pore size of the umbite structure that does not adsorb N_2. In addition, it has been reported that the adsorption of water occurs very slowly on this material.[26] Hence, umbite materials should have pore openings in the range of the water molecule size, justifying the high H_2/N_2 separation selectivity exhibited by our membranes. In general, Ti-umbite membranes perform better than Sn-umbite ones, from the point of view of both H_2 permeance (on average, $(1.2 \pm 1.9) \times 10^{-7}$ vs $(1.5 \pm 0.7) \times 10^{-8}$ mol/(m^2·s·Pa), respectively) and H_2/N_2 selectivity (on average, 22 ± 14 vs 15 ± 14, respectively), and as a consequence more effort has been devoted to them in this work. The average values used here are followed by their standard deviations. On the other hand, it is true that Ti-umbite membranes were prepared using different synthesis conditions (autoclave volume and position, seeding, in the oven, Ti source, washing) and even different kinds of supports. Thus when the statistic is made for the two most reproducible sets of Ti-umbite membranes, that is, from

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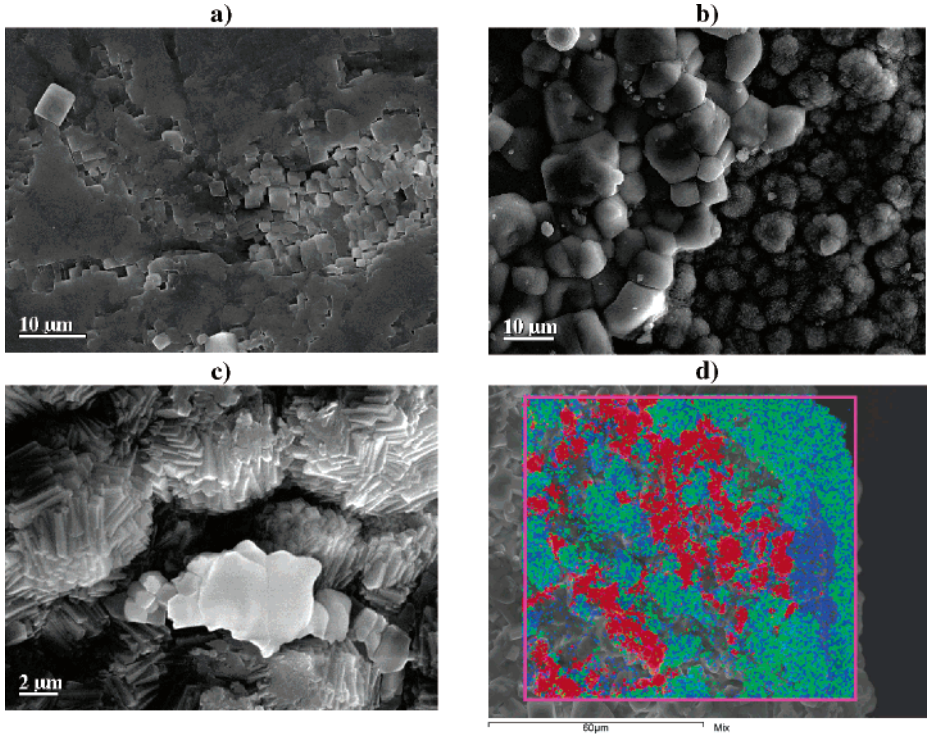

Figure 2. SEM images of an as-synthesized (before washing) Ti-umbite membrane: (a−c) top views and (d) X-ray map image of the cross section (green, red, and blue are for K, Al, and Si, respectively).

TiM2; TiM3; TiM4 and TiM5; and TiM8, TiM9, and TiM10, the average H_2 permeances are $(2.9 \pm 0.4) \times 10^{-8}$ and $(3.6 \pm 1.5) \times 10^{-8}$ mol/(m²·s·Pa), respectively, just a little larger than those for Sn-umbite membranes. In any event, among the umbite membranes, Ti-umbite membranes prepared on asymmetric TiO_2 supports are more reproducible and show the highest H_2/N_2 separation selectivities, always larger than 30 (on average, 39 ± 8). Several reasons can explain this fact. First, the TiO_2 supports have a smoother surface that should help to produce a more continuous membrane without intercrystalline defects, as can be inferred from Figure 1a,b for a Ti-umbite membrane (similar to TiM2) prepared on a symmetric alumina support and Figure 1c,d for a Ti-umbite membrane (similar to TiM8 and TiM9 to TiM11) prepared on a TiO_2 asymmetric support. A cross section of the latter (Figure 1e) gives a better idea of the membrane quality, showing a thickness of around 5 μm. Second, the chemical composition of the support, TiO_2 (a compound which was also used as a Ti source for Ti-umbite membrane synthesis, for instance, TiM5 in Table 2), should favor a more homogeneous and continuous nucleation and growth of the umbite crystals to form a membrane.

A third relevant issue is that, for all the membranes prepared on TiO_2 supports, the washing after synthesis was performed in a particular way which will be discussed below. Careful washing is important because the KCl excess (K^+ from KOH and KCl and Cl^- from $TiCl_3$, $SnCl_4$, and KCl) used in the synthesis gel (more so in the case of Ti-umbite) favors the cocrystallization of KCl and umbite (shown in Figure 2a−c for a membrane similar to TiM2, before washing). This cocrystallization gives rise to composite membranes in which the support is completely covered with a continuous and polycrystalline layer of umbite which in turn is coated with KCl crystals (Figure 2a,b). Therefore, this phenomenon occurs mainly at the end of the process, when the umbite membrane has already grown. However, Figure 2c shows how KCl may also crystallize between umbite particles, and in Figure 2d it is possible to see (in green) the presence of KCl throughout almost the whole cross section of the symmetric alumina support. Figure 1a−d, already discussed, corresponds to the surface of the membrane washed with water, where no KCl remains. Membrane TiM8 was flushed with water for only 1 min (with a washer flask) while membranes TiM9 to TiM11 were immersed at room temperature in 80 mL of acetone for 8 min. Thus, for these membranes the washing was less intensive than for the other membranes in Tables 1 and 2 (immersed in 80 mL of water for 1 h), particularly when acetone (where the solubility of KCl is negligible) was used.

However, Figure 3a shows that a membrane similar to TiM7, prepared on a symmetric alumina support, washed with acetone is almost completely clean of KCl. In fact, the acetone used (containing 0.3 wt % water) is able to dissolve at room temperature up to 0.06 g of KCl crystals per liter, as ascertained by inductively coupled plasma analysis. This means that the 80 mL of acetone employed per washing should be able to dissolve a relatively important amount of KCl, when compared to the weight gain of as-synthesized membranes which is in the 38−45 mg range. For membranes prepared on the rough symmetric alumina supports, the SEM analysis (Figure 1b) reveals that Ti-umbite grows as spherical caps. The lack of intergrowth between caps may be responsible for the presence of intercrystalline defects that eventually will be filled by KCl. Thorough washing may dissolve KCl between and on the umbite caps, resulting in a low performance membrane. Mild washing (for instance, with acetone) may only dissolve KCl crystallized on the caps releasing selectively umbite pores and giving rise to a

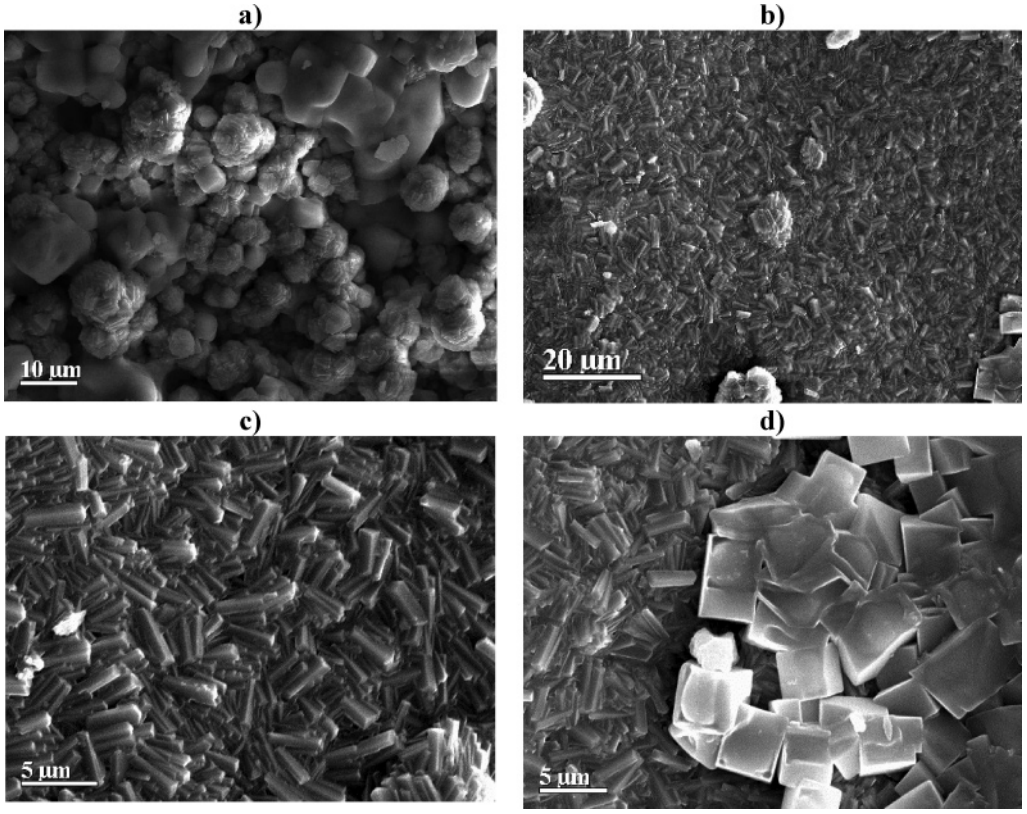

Figure 3. SEM images of top views of Ti-umbite membranes washed with acetone: (a) prepared on symmetric α-alumina supports and (b−d) prepared on TiO_2 asymmetric supports.

membrane with high H_2 separation selectivity. In the case of Ti-umbite prepared on TiO_2 supports the situation is better, even if KCl is also formed. As discussed above, the layer of the desired material is more uniform and continuous, and the washing with acetone (for a membrane similar to TiM7, TiM9, and TiM10) produces very clean surfaces (Figure 3b), even if some KCl may remain in some places (Figure 3c). Of course, thorough water washing of these membranes may also produce defects, as shown in Figure 1d. Another difference between TiO_2 and α-alumina supports is that in the former the support pores are largely spared from filling with the gel during the hydrothermal synthesis, as a result of the size of the pores exposed to the solution (only 5 nm). In contrast, α-alumina supports expose to the solution pores of 1900 nm which are easily penetrated by solution containing KCl, whose crystallization inside the support or migration to the surface during the washing and drying stages may damage the membrane.

Figure 4 shows the effect of the washing with acetone on the performance of membrane TiM10. After the first washing, the H_2 permeance reaches the constant value of 4.5×10^{-8} mol/(m²·s·Pa), while the H_2/N_2 selectivity increases up to the third washing, after which it decreases. Before the plateau is attained, KCl is dissolved from the umbite membrane surface, releasing selective pores. At the plateau, KCl is dissolved from the spaces between the umbite crystals (or spherical caps in the case of Ti-umbite prepared on symmetric alumina supports) releasing nonselective pores. As a result of their relatively large size (compared to those of umbite), these nonselective pores could be eventually blocked by either solvent molecules (because the membranes are only pretreated at 170 °C before the permeance tests) or

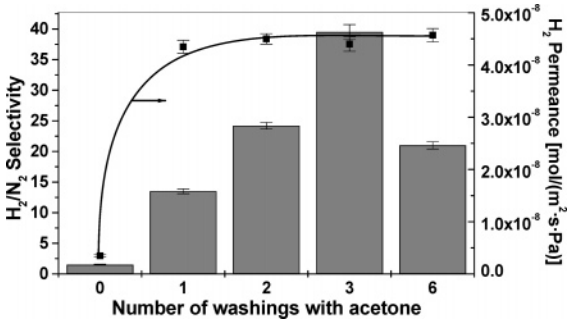

Figure 4. H_2/N_2 separation selectivity and H_2 permeance through membrane TiM10 as a function of the number of acetone washing cycles.

recrystallized KCl, which would explain the decrease of the N_2 permeance and the constant level of H_2 permeance displayed in Figure 4. We do not speculate on the dissolution of umbite because this material is much less soluble than KCl. With a further washing, some KCl deposits plugging intercrystalline defects on the membrane are removed, and the selectivity decreases. The performance of TiM7 was also evaluated against the number of washings with acetone: a maximum H_2/N_2 selectivity of 19 was obtained after the fourth washing.

Washing with acetone is also a way of mildly dehydrating the umbite membrane, which contrasts with the usual treatment at 100 °C carried out before the permeance tests at 170 °C. Obviously, the higher the membrane water content the more the thermal treatments may affect (upon dehydration) the membrane structure. As a consequence, dehydration of the umbite membrane with acetone should improve its stability.

Finally, while it is true that different conditions were employed for the synthesis of the Ti-umbite membranes (auto-

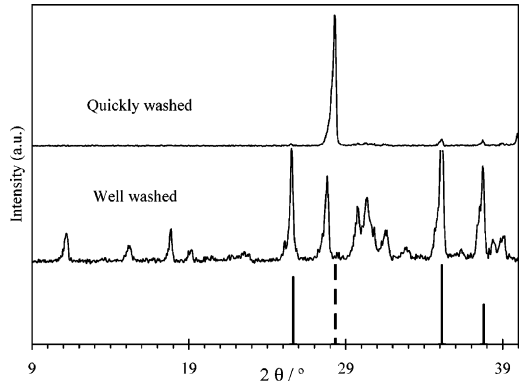

Figure 5. XRD patterns of Ti-umbite membranes: quickly washed with a washer flask and held for 10 s under sonication in water and well-washed with water. The dashed and solid lines depict KCl and α-alumina support reflections, respectively.

clave position and volume, seeding, etc.), the two factors having a determinant influence on the separation properties are the type of support and the washing conditions. On one hand, TiO_2 supports are preferred over α-alumina ones because they reproducibly result in the best membranes. On the other hand, the washing with acetone provides a much better control of the dissolution of KCl formed on the membrane, as shown in Figure 4. The autoclave volume also has its effect as can be inferred from a comparison of membranes TiM2, TiM3, and TiM4, maintaining a level of H_2 permeance of about $2-4 \times 10^{-8}$ mol/(m^2·s·Pa) as the H_2/N_2 selectivity increases from 8.1 to 19 when the volume of gel involved increases from 35 to 140 mL. Assuming that there is a competition to consume the synthesis gel between the support and the gel itself, a higher gel/support ratio should help to reduce the concentration gradients across the autoclave (for these three membranes the synthesis was vertical without rotation), increasing the crystallinity of the membrane.

Characterization of Umbite Membranes by XRD. The XRD patterns of Sn- and Ti-umbite membranes washed with water by means of a washer flask and sonicated for 10 s display strong reflections from KCl, while the patterns of the same samples after thorough washing with water reveal that pure umbite is the only phase present on the surface of the supports, indicating the cocrystallization of KCl and umbite (Figure 5 for the Ti-umbite membrane prepared on symmetric α-alumina supports). Some peaks coming from the support are also present in the pattern. As expected, the reflections of membranes and powders appear at the same 2θ values (Figure 6 for Ti-umbite membranes on TiO_2 supports). However, because of preferential orientation effects, the intensity of some peaks is significantly different for the powder and membrane forms. The indexes of Ti-umbite reflections in Figure 6a were calculated by PCW[27] using unit cell parameters and atomic coordinates of Ti-umbite taken from the literature[14] and assuming an orthorhombic unit cell, with space group $P2_12_12_1$. For the membrane prepared without rotation (Figure 6b) the intensity of the (200) peak at about 17.84° 2θ increases significantly

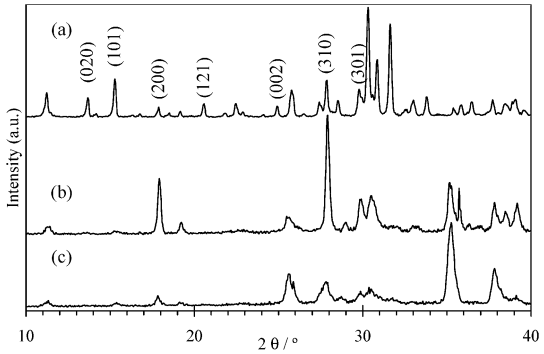

Figure 6. XRD patterns of Ti-umbite powder (a) and membranes prepared on TiO_2 asymmetric supports without (b) and with (c) rotation.

suggesting an *a* out-of-plane preferential orientation, while the intensities of the (020) and (002) reflections at about 13.64 and 24.96° 2θ, respectively, decrease significantly, indicating that the *b* and *c* axes are in-plane, in accordance with an *a* out-of-plane preferential orientation. For the membrane prepared in a rotating autoclave (Figure 6c), the signal of (200) has a much lower intensity, indicating a less marked preferential orientation, as expected.

To quantify the orientation degree, the so-called crystallographic preferred orientation index, CPO, was calculated. The CPO based on peaks X and Y is defined as $CPO_{X/Y} = ((I_X/I_Y)_m - (I_X/I_Y)_p)/(I_X/I_Y)_p$,[28] where *I* is the integrated intensity of the corresponding reflections and *m* and *p* refer to the membrane sample and powder reference, respectively. The calculated $CPO_{200/020}$ is 72 and 30 for membranes prepared without and with rotation, respectively, indicating a stronger *a* out-of-plane preferential orientation for membranes obtained without rotation. The orientation effect also results in a significant intensity change of the reflections, such as about 15.2 (101), 20.3 (121), 27.7 (310), and 29.3° (301) 2θ. Although crystals in an oriented membrane may intergrow better, because the one-dimension eight-membered ring channel in umbite materials is perpendicular to direction *a*, the increasing *a* out-of-plane preferential orientation may be detrimental to the permeance of the membranes and affect their gas separation properties. This could partially explain why membrane TiM8 performs better than membranes TiM9, TiM10, and TiM11 (all of them prepared on TiO_2 supports, see Table 2). On the other hand, if the *c* out-of-plane oriented membrane could be prepared, the intergrowth of crystals and the permeance of the membrane would be improved.

Separation of H_2 Containing Mixtures through Umbite Membranes. Figure 7 shows the H_2 permeance and the H_2/N_2 separation selectivity as a function of temperature for Ti-umbite membrane TiM8. The permeance of H_2 is higher than that of N_2 in the 30−150 °C temperature range. As expected considering the microporous character[25] of these membranes, both permeances are activated; that is, they increase with

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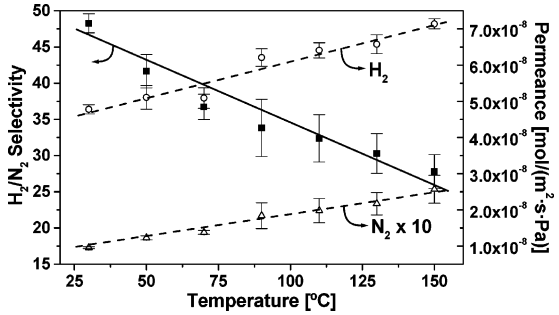

Figure 7. H_2/N_2 separation selectivity and H_2 and N_2 permeances through membrane TiM8 as a function of temperature.

Table 3. Separation of Mixtures Containing H_2 through Membrane TiM8

run no.	mixture	time under stream at 30−170 °C [h]	H_2 permeance $\times 10^8$ [mol/(m²·s·Pa)]	selectivity
1	H_2/N_2	fresh membrane	4.78 ± 0.18	48.2 ± 1.3
2	H_2/propane	120	6.35 ± 0.28	46.5 ± 1.8
3	H_2/CO_2	136	11.4 ± 0.4	30.9 ± 0.7
4	H_2/N_2	148	10.9 ± 0.4	31.5 ± 0.8
5	H_2/N_2	153[b]	3.67 ± 0.20	205 ± 3
6	H_2/N_2	230	5.71 ± 0.14	55.7 ± 2.8
7	H_2/N_2	640	5.22 ± 0.13	42.0 ± 1.4
8	H_2/N_2	644[c]	8.38 ± 0.13	31.4 ± 0.5

[a] The permeances are given at 60 °C. [b] The H_2/N_2 mixture was saturated in water at room temperature for the next 63 h. [c] Pressure drop = 1 bar.

increasing temperature. The H_2/N_2 selectivity decreases with temperature because the N_2 permeance increases faster than that of H_2. This different temperature activation may be explained assuming that H_2 and N_2 permeate through pores of different size: N_2 does not enter the umbite channel; it permeates only through intercrystalline defect pores. These defects should be of a size similar to that of the N_2 molecule, otherwise such a high separation selectivity and activated transport would not be observed for the permeating molecules (even for N_2 whose transport for these membranes is allowed only through defects). Regarding this point, it is well-known that, for the widely studied silicalite membranes,[29] the activation energy for diffusion, calculated from permeability data, is considerably higher for SF_6, a molecule with a kinetic diameter similar to the pore size of silicalite, than for N_2, whose kinetic diameter is smaller than the zeolite pores (0.55 nm). In the case of the umbite membranes the N_2 permeance would be more activated with temperature through pores (defect pores) of size very similar to its kinetic diameter (0.364 nm), while the smaller kinetic diameter of the H_2 molecule (0.289 nm) would lead to a less activated permeation (through both umbite pores and defect pores).

Table 3 shows that membrane TiM8 is also able to separate H_2 from its mixtures with CO_2 or propane. Because the level of H_2 permeance observed with these mixtures is comparable or even higher than that of the mixture with N_2, CO_2 and propane molecules are not adsorbed on the umbite pores which would have hindered the H_2 permeance. Moreover, the smaller (0.33 nm) CO_2 molecule permeates faster than N_2 or propane (0.43 nm) reducing the selectivity (30.9 for CO_2 vs 31.5−48.2 and 46.5 for N_2 and propane, respectively). All these results should be considered together with the fact that, with time on stream (see Table 3) the H_2 permeance increases (in run 4, it increases after 148 h from 4.78 to 10.9 $\times 10^{-8}$ mol/(m²·s·Pa)) while simultaneously the H_2/N_2 selectivity decreases (from 48.2 to 31.5). This strongly suggests that either new nonselective pores were created or the pore size increased, perhaps because of water content stabilization in the umbite membrane. Runs 4−7 in Table 3 agree with the hypothesis concerning the hydration of the membrane: at 153 h the H_2/N_2 feed was saturated in water, this situation being maintained for the next 63 h after which the membrane was heated for 14 h at 170 °C in Ar flow. During this 63 h period, first, because of water capillary condensation, the H_2 permeance decreased while the H_2/N_2 selectivity increased; second, the membrane was re-hydrated; and after 230 h (run 6, now without water) both H_2 permeance and H_2/N_2 selectivity were 5.71 $\times 10^{-8}$ mol/(m²·s·Pa) and 55.7, respectively. After 640 h (run 7) these were 5.22 $\times 10^{-8}$ mol/(m²·s·Pa) and 42.0, respectively; that is, the membrane recovered a level of performance similar to that of run 1. Finally, even if working with sweep gas was preferred, for comparison, membrane TiM8 was also tested under a pressure drop of 1 bar (run 8) giving a H_2 permeance of 8.38 $\times 10^{-8}$ mol/(m²·s·Pa) together with a H_2/N_2 selectivity of 31.4, while this membrane performed with no pressure gradient (run 7, because this is the nearest) with a permeance of 5.22 $\times 10^{-8}$ mol/(m²·s·Pa) together with a H_2/N_2 selectivity of 42.0. Finally, Table 4 shows some significant examples of the H_2/N_2 separation through zeolite membranes. From the data presented, it can be said that umbite membranes are among the best performing zeolite membranes for H_2/N_2 separation.

Table 4. Separation of the H_2/N_2 Mixture through Zeolitic Membranes

Zeolite	temperature [°C]	H_2 permeance $\times 10^8$ [mol/(m²·s·Pa)]	H_2/N_2 selectivity	ref
Zeolite A	35	0.8	4.6	30
ZSM-5	50	2.6	38	31
Fe-ZSM-5	25	300	3.3	32
ZSM-5[a]	110	2.0	100	33
Ti-umbite	60	6.2	39	this work[b]

[a] Modified by catalytic cracking of silane. [b] Average for the four membranes prepared on TiO_2 supports.

Conclusion

Microporous stannosilicate ($K_2SnSi_3O_9 \cdot H_2O$) and titanosilicate ($K_2TiSi_3O_9 \cdot H_2O$) with an umbite structure (revealed by XRD) can be prepared as continuous membranes on porous α-alumina and TiO_2 tubular supports by seeded hydrothermal synthesis. It has been observed that Ti-umbite membranes perform better than Sn-umbite ones. Although different synthesis conditions (autoclave position, seeding, etc.) have been used to prepare the Ti-umbite membranes,

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the two main factors influencing the separation properties are the support and washing conditions. TiO_2 is preferred over α-alumina supports because it more reproducibly yields the best membranes. Gentle washing with water or acetone allows a careful control of the dissolution of KCl cocrystallized on the membrane and, as a consequence, of the performance of the membranes in the separation of H_2 containing mixtures. These membranes, which may after 640 h under stream separate the H_2/N_2 mixture with selectivities higher than 30 together with permeations in the 10^{-7} mol/(m^2·s·Pa) range, show a time-dependent performance. They eventually undergo some kind of structural change, probably related to the water content stabilization, that decreases their separation ability. This decrease can be reversed by rehydration of the membrane.

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