Textural Stability of Titania–Alumina Composite Membranes

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Textural evolution (porosity reduction, pore and crystallite growth) in titania–alumina composite membranes has been studied using thermal analysis, X-ray diffraction, field emission scanning electron microscopy and N_2 physisorption techniques. The presence of alumina in the membranes improved the thermal stability of the porous texture by retarding the anatase-to-rutile phase transformation and grain growth of the anatase phase. Pure unsupported titania membranes lose their porosity completely after calcination at 600 °C for 8 h, whereas the titania–50 wt.% alumina composite membranes retained a porosity of ca. 40% even after calcination for 30 h at 800 °C. The anatase-to-rutile phase transformation temperatures for pure unsupported titania and the titania phase of the unsupported titania–alumina composite membranes (50 wt.% alumina) were found to be 580 and 960 °C, respectively, as observed from the DSC data.

From XRD results it was found that pure unsupported titania and the unsupported titania–alumina (50 wt.% alumina) composite membranes transformed to more than 95% of rutile after heat treatment for 8 h at 600 and 900 °C, respectively. The anatase to rutile phase transformation kinetics were studied using DSC data and applying a non-isothermal form of the Avrami equation.

Keywords: Ceramic membrane; Titania; Alumina; Composite; Textural stability

Differences in the textural evolution, porosity reduction and pore growth, and the phase transformation behaviour between supported and unsupported titania membranes were investigated and reported elsewhere.^{1,2} In titania membranes, one of the main mechanisms of porosity and surface-area reduction is the enhanced sintering during the anatase-to-rutile phase transformation, which is also accompanied by grain growth.^{1–3} Below 500 °C the amount of porosity and surface-area reduction due to anatase crystallite growth and hydrothermal sintering is small compared to the drastic reduction caused by the enhanced densification during the anatase-to-rutile phase transformation.¹ The pore growth and porosity reduction in titania membranes can be retarded by retarding the anatase crystallite growth (before the phase transformation),¹ or by retarding (or avoiding) the phase transformation or both. It is known from the literature that the presence of oxides like alumina and lanthana in titania decreases the grain growth during initial stage of sintering and also retards the anatase-to-rutile phase transformation.^{1,4} In this paper results on the textural evolution of titania–alumina composite membranes containing 3, 6, 9 and 50 wt.% alumina are presented. The volume fractions of alumina present in the composite membranes are almost the same as the weight fractions due to similar densities of the anatase phase of titania and of α -alumina (3.9 g cm^{-3}). The presence of alumina, as for lanthanum oxide,¹ in titania membranes is expected to retard the crystallite growth and phase transformation and thereby improve the textural properties at high temperatures. The properties discussed here are evaluated using unsupported membranes unless otherwise mentioned.

Besides their increased textural stability (compared with pure titania), composite membranes of e.g. alumina–titania are of interest because they are easier to form than pure titania, especially for greater thicknesses.^{5–7} These phenomena require a minimum amount of alumina of ca. 50 wt.%, which makes this composition of particular interest. In this context, 'easy to form' means that the probability of making a crack-free and pin-hole-free membrane is higher.

Experimental

Composite Precursor Sol and Membrane Preparation

Titania–alumina composite membranes were synthesized from a two-component sol made by mixing dropwise with stirring 1 mol dm^{-3} boehmite sol with 0.3 mol dm^{-3} titania sol in the appropriate ratio to obtain composite membranes containing 3, 6, 9 and 50 wt.% of alumina. Fig. 1 illustrates the important steps involved in the preparation of the two-component sol. Boehmite sol was prepared from aluminium *sec*-butoxide and titania sol was prepared from titanium isopropoxide. In both cases the sols were electrostatically stabilized with HNO_3 . Alumina and titania precursor sols had concentrations of 1 and 0.3 mol dm^{-3} and pHs of ca. 4 and 2, respectively. The composite precursor sol had a pH in the range 2–3. Detailed experimental procedures were reported elsewhere.^{5,6,8}

Supported and unsupported membranes were made from the two-component sol as described in detail in a previous publication.² Supported membranes were formed on porous α -alumina supports (40–45% porosity and average pore diameter of 160 nm) in a single dipping process. All the membrane samples were dried at 40 °C and 60% relative humidity (RH) till the weight of the membrane remained constant. After drying supported and unsupported membranes had thicknesses of ca. 6 and 15 μm , respectively. Further calcinations were carried out at temperatures ranging from 600 to 900 °C for either 8 or 30 h. After calcination the shrinkage in the thickness direction was found to be up to 20 and 5%, depending on the calcination temperature, for supported and unsupported membranes, respectively. Unsupported membranes were calcined with a heating rate of 100 °C h^{-1} and furnace cooled. Supported and some unsupported (for comparison) membranes were calcined at 900 °C with heating and cooling rates of 15 and 30 °C h^{-1} , respectively.

Thermal Analysis

Differential scanning calorimetric studies were performed, using a Polymer Lab. Thermal Science system, at heating

Fig. 1 Flow chart showing the important steps in the preparation of titania, alumina and titania-alumina composite membrane precursors

rates ranging from 5 to 20 °C min⁻¹. DTA and TG runs were performed at a heating rate of 10 °C min⁻¹. All the thermal analyses experiments were performed using alumina cups with a sample weight of 40 ± 2 mg. The reference material was precalcined α -alumina.

X-Ray Diffraction

X-Ray diffraction patterns were recorded using a Philips diffractometer (PW 1710) with Cu-K α radiation in the step-scan mode with a 2θ range of 23–46°. The scanning was performed in steps of 0.015° 2θ with an interval of 10 s. Crystallite size and the relative amounts of anatase and rutile phases present were calculated from the (101) reflection of anatase and the (110) reflection of rutile, which are separated by ca. 2° (2θ) with good resolution. To measure accurately the integrated intensity and the width at half maximum a pattern-fitting technique was applied.⁹ To carry out the fit, a Marquart non-linear least-squares algorithm was used.¹⁰ The instrumental and wavelength-related broadenings were corrected by assuming a Cauchy relationship.¹¹ Cauchy approximation accounts only for size-broadening and the presence of strain is neglected. The crystallite size of anatase and rutile phases were calculated using the Scherrer relationship:

$$D_{hkl} = K\lambda / (B_{hkl} \cos\theta) \quad (1)$$

where B_{hkl} is the width of the peak at half maximum and λ is the wavelength of Cu-K α . The value of K varies from 0.9 to

1.4 depending on many factors including the shape of the primary crystallite.¹¹ In this study a value of 1.38 is assumed for K . This K value accounts for the deviation from pure Cauchy behaviour. The crystallite sizes calculated with this value of K are in good agreement with the sizes calculated from FE-SEM micrographs in the lower temperature range. However, the alumina-containing titania samples calcined above 600 °C do not show appreciable deviation from the pure Cauchy behaviour. This is probably because the line broadening does not contain contributions from residual stress or inhomogeneities (microstrains). In that situation a K value of 1.38 will give slightly exaggerated values for the crystallite size.

The fraction of rutile present in the membranes after various heat treatments were calculated using the equation¹²

$$W_R = 1 / [1 + 0.8(I_A/I_R)] \quad (2)$$

W_R is the weight fraction of rutile while I_A and I_R are the X-ray integrated intensities of the (101) reflection of anatase and the (110) reflection of rutile, respectively. The integrated intensity was calculated after correcting for instrumental and wavelength related broadenings.

Electron Microscopy

Titania, alumina and titania-alumina composite membranes were subjected to a high-resolution field-emission scanning electron microscopic (FE-SEM) study using a Hitachi S-900 SEM. The field-emission electron source consists of a pointed cathode and two anodes. The cathode is made of a single-crystal tungsten tip polished to 100 nm in radius of curvature. The emission intensity is of the order of 10⁵ A cm⁻² which is very high when compared with 10 A cm⁻² of conventional thermionic sources such as a tungsten hairpin type filament. Because of the high emission intensity in the field emission, there is sufficient current available to allow excellent resolution with good signal-to-noise ratio. The specimens were made conducting by coating with platinum. The pictures were made at magnifications ranging from 50 000 to 200 000 ×.

Physical Adsorption Measurements

N₂ adsorption/desorption measurements were carried out at liquid-nitrogen temperature in a Micromeritics ASAP 2400 system. All the samples were degassed at 90 °C prior to the actual adsorption/desorption measurements. The BET constant was in the range 100–200, indicating that the monolayer-multilayer adsorption mechanism occurs, which allows us to apply the BET model to evaluate the surface area. All the isotherms were a typical type IV (BDDT classification)¹³ with a type E hysteresis. There was very little or no microporosity present in these membranes.

Results and Discussion

Phase Stability

Fig. 2 shows the DSC peak temperatures corresponding to the anatase-to-rutile transformation at different heating rates for unsupported titania membranes containing 0, 3, 6, 9 and 50 wt.% alumina (xerogel thickness = 15 μ m). At any given heating rate the transformation temperature of the alumina-containing membranes is more than 300 °C higher than that of pure titania. Springer and Yan⁴ have also noticed the influence of alumina in retarding the phase transformation and grain growth of titania. The peak temperature increased with increasing alumina content for alumina-doped membranes. It should be noted that the anatase-to-rutile phase

Fig. 2 DSC peak temperatures of the anatase-to-rutile transformation of titania membranes containing (+) 0, (●) 3, (○) 6, (▽) 9 and (□) 50 wt.% of alumina

transformation is a metastable-to-stable transformation and, in a strict sense, there is no real phase transformation temperature, as in the case of an equilibrium reversible transformation (one stable phase to another stable phase). The peak temperature obtained from DSC runs are simply the temperature at which the transformation rate is the highest. For all practical purposes the difference in the DSC transformation temperatures is a rough indication of the extent of retardation of the phase transformation.

X-Ray diffraction patterns of unsupported titania-(50 wt.%)alumina membranes calcined for 8 h at different temperatures are given in Fig. 3. The peaks marked A, TA, and TR represent α -alumina, anatase, and rutile phases, respectively. The two diffraction lines of α -alumina are the (104) and the (113) peak; anatase is represented by the strong (101) peak at $2\theta = 25.6^\circ$ and by three reflections between $2\theta = 36$ and 39° [(103), (004) and (112) peaks]. The five main reflections of rutile shown in Fig. 3 are the (110), (101), (200), (111) and (210) peaks. Up to 700 °C there is only anatase present, and at 800 °C some new peaks, corresponding to rutile, start appearing. By 900 °C the titania part of the membrane contains more than 95% rutile. As mentioned above there is no sharp transformation temperature. Pure titania membranes transform to more than 95% rutile by 600 °C, which is *ca.* 300 °C less than that of the composite, under the same calcination conditions (heating rate = 100°C h^{-1} ; 8 h soaking).¹ This temperature difference is smaller than, as expected, that obtained from the DSC results given in Fig. 2.

Fig. 3 XRD pattern of unsupported titania-(50 wt.%)alumina composite membranes heated at 600(d), 700(c), 800(b) and 900 °C(a) for 8 h (TA = anatase titania, TR = rutile titania and A = α -alumina)

Crystallite and Pore Growth and Porosity Reduction

The data on crystallite sizes, calculated from eqn. (1), at different calcination temperatures of the titania phase of the unsupported membranes containing different amounts of alumina are given in Fig. 4. All the samples were calcined for 8 h. At any given temperature the crystallite size of anatase decreased with an increasing amount of alumina. At 800 °C the difference in the crystallite sizes between membranes containing less than 10 wt.% alumina and the 50 wt.% alumina containing composite membranes increased, the crystallite sizes of 9 and 50 wt.% alumina containing titania membranes being 43 and 29 nm, respectively.

Fig. 5 gives the pore growth data of alumina-containing titania membranes, heated at different temperatures, containing different amounts of alumina. The pore diameters were calculated from the desorption branch of the isotherm. At any given temperature the pore size increases with a decreasing amount of alumina. Pore growth in the membrane containing 50 wt.% alumina is very little up to 800 °C. By 900 °C the pore grows to *ca.* 36 nm in diameter. Table 1 gives

Fig. 4 Crystallite sizes of the anatase phase of unsupported titania membranes containing (+) 3, (○) 6, (▲) 9 and (▽) 50 wt.% of alumina heated at different temperatures for 8 h

Fig. 5 Pore growth versus temperature of unsupported titania membranes containing (+) 3, (○) 6, (▲) 9 and (▽) 50 wt.% of alumina

Table 1 Percentage porosities and pore diameters in mm (given in brackets) calculated from the desorption branch of the isotherm of titania membranes containing different amounts of alumina

T/°C	wt.% of alumina				
	3	6	9	50	100
600 (8 h)	30 (5.2)	30 (4.4)	33 (4.2)	33 (3.4)	46 (4)
700 (8 h)	29	31	34	39	45
800 (8 h)	20	30	33	40	49
800 (30 h)	15 (18)	20 (17)	24 (18)	40 (8.8)	
900 (8 h)	6	8	10	36	49

the porosities of titania membranes containing different amounts of alumina. For the membranes containing less than 10 wt.% alumina, porosity decreased (or remained more or less the same) with increasing calcination temperature and time. The porosity of membranes containing 50 wt.% alumina increased till 800 °C; it retained a porosity of *ca.* 36% even at 900 °C. The initial increase in the porosity may be attributed to the negative volume change of the alumina phase in the membranes. Alumina is initially present in the composite as boehmite and is expected that it will convert to γ -alumina and finally to α -alumina on heat treatment, this conversion is accompanied by a volume change of *ca.* 20%. These phases were not observed in the X-ray pattern given in Fig. 3. Only a very small peak corresponding to α -alumina can be seen at 900 °C. The porosity of titania membranes containing 9 wt.% alumina remains the same up to 800 °C (8 h) and decreases to *ca.* 20% when calcined at 800 °C for 30 h.

Fig. 6 gives the pore size distribution of titania membranes containing different amounts of alumina heated at 600 °C for 8 h. It can be seen that with an increase in the alumina content the distribution becomes sharper. The sharpest distribution is observed in the case of the membrane containing 50 wt.% alumina. Fig. 7 gives the pore size distribution of the composite membrane containing 50 wt.% alumina heated at different temperatures and times. With an increase in calcination temperature the distribution becomes broader, the membrane calcined at 800 °C for 30 h having the broadest distribution.

Phase Transformation Kinetics

One of the main causes of pore growth is the enhanced sintering during the anatase to rutile transformation.¹ The

Fig. 6 Pore size distribution of titania membranes, calcined at 600 °C for 8 h, containing (+) 3, (○) 6, (▲) 9 and (▽) 50 wt.% of alumina

Fig. 7 Pore size distribution of titania-alumina composite membranes containing 50 wt.% alumina, calcined at (+) 600/8, (○) 700/8, (▲) 800/8 and (▽) 800 °C/30 h

non-isothermal DSC data given in Fig. 2 can be treated using a non-isothermal Avrami relation.¹⁴ This equation derived by Bansal *et al.* based on the basic equation of the Avrami model is

$$[(T_p^2/\phi)A]/(E/R) = \exp(E/RT_p) \quad (3)$$

where A is the frequency factor, T_p is the DSC peak temperature and E is the equivalent activation energy, calculated from the Avrami model; R is the universal gas constant, and ϕ is the DSC heating rate. A plot of $\ln[T_p^2/\phi]$ vs. $1/T_p$ will give a straight line with a slope of E/R . From the slope and the intercept, E and A can be determined. Table 2 gives the parameters obtained from the Avrami analysis of the data given in Fig. 2. The activation energies of the transformation are *ca.* 213 kJ mol⁻¹ for pure titania and *ca.* 380 kJ mol⁻¹ for the titania-alumina composite membrane. This higher activation energy of the phase transformation of titania in the composite membranes causes the slower transformation kinetics, especially at moderate temperatures. It should be noted that no signal corresponding to the transition of γ -alumina was observed in the DSC trace of the composite membranes.

Effect of Alumina on the Textural Stabilization of Titania Membranes

It is known from the literature that alumina retards the crystallite growth of titania and also the anatase-to-rutile transformation.⁴ Fig. 8 gives the amount of rutile present, calculated using eqn. (2), in the titania membranes containing different amounts of alumina. At temperatures higher than 700 °C there is a sharp increase in the amount of rutile present in the membranes. The same trend can be seen in the pore growth data given in Fig. 5. In the case of composite membranes the pore growth with temperature is less drastic till 800 °C. By 900 °C all the membranes contain more than 95% of rutile (Fig. 8) and pores of the membranes containing 3, 6 and 9 wt.% alumina have grown to larger than 40 nm (not shown in Fig. 5) while the porosities are <10%. At 900 °C the composite (50 wt.% alumina) membrane retains a porosity

Table 2 Parameters from the non-isothermal Avrami analysis^a

	$E/\text{kJ mol}^{-1}$	$10^{-7} A/\text{s}^{-1}$	correlation coefficient
pure titania	213	2.7	0.993
Ti-Al (3 wt.%)	375	4.5	0.996
Ti-Al (6 wt.%)	382	4.6	0.999
Ti-Al (9 wt.%)	385	4.6	0.998
Ti-Al (50 wt.%)	380	4.6	0.995

Fig. 8 Amount of rutile present in the titania membranes containing (+) 3, (○) 6, (▲) 9 and (▽) 50 wt.% of alumina heated at different temperatures for 8 h

Fig. 9 Porosity contributed by the titania phase in the composite membranes containing (+) 3, (○) 6, (▲) 9 and (▽) 50 wt.% of alumina heated at different temperatures for 8 h

of *ca.* 20% with a pore diameter <40 nm. At any given temperature the absolute porosity of the titania membranes containing different amounts of alumina (Table 1) is found to increase with an increase in the alumina content. This increase can be due to two reasons: (1) porosity of pure alumina at any given temperature above 600 °C is higher than that of pure titania, which is completely dense at 600 °C;¹ (2) titania will retain some porosity due to the stabilizing action of alumina. The porosity contributed by the titania phase, P_T , in the titania-alumina membranes can be calculated using a simple rule of mixtures:¹⁵

$$P_T = [1/(1-n)] (P_{TA} - nP_A) \quad (4)$$

where P_{TA} and P_A are the measured porosities of titania membranes containing alumina and of pure alumina membranes, respectively. n is the weight fraction of alumina present in the membranes, $n=0.03, 0.06, 0.09$ and 0.50 . Eqn. (4) is valid only if the presence of titania does not affect the textural stability of alumina. If the presence of titania improves the textural stability of alumina, then the calculated value of P_T will be more and if it destabilizes, the calculated value of P_T will be less than the actual porosity contribution of the titania phase. Fig. 9 gives the porosity contributed by the titania phase, calculated from Table 1 using eqn. (4), in the membranes containing different amounts of alumina. The

porosity contribution of the titania phase increased with the amount of alumina present in the membranes. At 900 °C the porosity contributed by the porous titania phase of the 50 wt.% alumina containing composite membrane is *ca.* 25 and is clearly much higher than that of the composite membranes with $n=0.06$ and 0.09 .

From the above discussion it is clear that the presence of alumina in titania membranes resulted in the retardation of crystallite growth (Fig. 4) and phase transformation. This resulted in consequent stabilization of the porous texture. That is the pore growth and porosity reduction has been retarded by alumina. The extent of this retarding effect increased with increasing alumina content.

Comparison of Supported and Unsupported Composite Membranes

It has been clearly shown that there is a considerable difference in sintering and phase transformation behaviour between supported and unsupported membranes.² This difference can be attributed to a combination of many different effects. The most important among them is the constraint caused by the rigid support. This retards both sintering (pore growth, crystallite growth and porosity reduction) and phase transformation, which in turn reduces the contribution, on the porosity reduction, by the enhanced sintering during the phase transformation. Pure titania membranes lose their porosity completely when calcined at 600 °C for 8 h, whereas the supported counterpart retained *ca.* 30% porosity at 700 °C (8 h). Unsupported titania-(50 wt.%)alumina composite membranes retained a porosity of *ca.* 40% at 800 °C, 8 h. Then it is expected that the supported membrane of the same composition would retain at least that much porosity at 900 °C. This can be verified by comparing the high-resolution electron micrographs of the supported and unsupported composite membranes heated at 900 °C for 8 h (Fig. 10). From the micrographs not much difference in the porosities between supported and unsupported membranes are observed. The supported membrane seems to have a narrow pore size distribution compared with the unsupported counterpart. At these temperatures the effect of the composite composition on the structural stability of the membranes seems to be larger than the effect of support constraint.

Fig. 10 FE-SEM micrographs of (a) supported and (b) unsupported membranes calcined at 900 °C for 8 h

The supported membrane has a more uniform crystallite size distribution, in the range 15–20 nm, compared to the unsupported counterpart. In the unsupported membranes crystallites of two different sizes can be seen. The smaller crystallites, in the range 15–20 nm, represent the alumina phase and the larger ones, in the range 40–50 nm, represent rutile particles of the titania phase.

Conclusions

Titania–alumina(50 wt.%) composite membranes showed an improved textural stability compared to pure titania membranes. The porosity of pure titania above 600 °C is immeasurably small, whereas the titania–alumina composite membrane has *ca.* 40% porosity with an average pore diameter of 9 nm after heat treatment at 800 °C for 30 h.

The anatase-to-rutile transformation temperature of the composite membrane (50 wt.% alumina) obtained from DSC was more than 300 °C higher than that of pure titania. The non-isothermal Avrami activation energies were found to be 213 and 380 kJ mol⁻¹ for pure titania and titania–alumina composite membranes, respectively.

The presence of alumina in the composite membranes decreased the grain growth of the anatase phase and retarded the anatase to rutile transformation. Both these effects contributed to the stabilization of the porous texture of the titania phase.

Crystallite growth in the supported membrane is retarded by the constraint exerted by the rigid support.

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