Synthesis and Characterization of Microporous Titania Membranes

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Abstract. A procedure for the preparation of microporous titania membranes by the polymeric sol-gel technique is reported. The influence of acid/titanium ratio, water/titanium ratio, method of mixing components and refluxing time on particle size and sol stability was investigated. The thermal evolution, structural characteristics and liquid permeation properties of calcined materials were studied. Highly reproducible amorphous microporous titania layers with pore sizes ≤ 0.8 nm were obtained on both mesoporous γ-alumina and titania/zirconia coated substrates. The upper limit of thermal stability of the amorphous phase is $\sim 300^\circ$C. Higher calcination temperatures led to phase transformation into anatase, which was accompanied by a collapse of the microstructure. The material was found to be chemically stable in a wide pH interval.

Keywords: titania, polymeric sol, membrane, microporous, amorphous

1. Introduction

Microporous ceramic membranes have a high application potential due to their chemical, mechanical and thermal stability. One of the most widely used methods for the preparation of microporous membranes with different structures in the last decades has been sol-gel processing. For the preparation of microporous materials with a pore size smaller than 2 nm the polymeric sol-gel technique has been suggested [1–7]. With this method a network of partially hydrolyzed and polycondensed oligomers diluted in the solvent is formed. A microporous structure is obtained upon layer application (coating), drying and calcination.

Many research groups have studied microporous membranes made of amorphous silica with pore sizes of 0.3–0.5 nm [8–10]. Although silica membranes show good performance in gas separation [8] and pervaporation [9, 10], its hydrothermal and chemical stability is limited. Amorphous microporous titania is expected to exhibit a better performance in these respects [11–14].

In this study a procedure for the preparation of microporous titania membranes by the polymeric sol-gel technique is reported. The influence of several processing variables on particle size and sol stability was investigated. Additionally, the thermal evolution, structural characteristics and liquid permeation properties of calcined powders and films were studied.

2. Experimental

Polymeric titania sols were prepared in accordance with the general procedures outlined by Livage et al. [1]. Titanium tetra-ethoxide (Aldrich) was used as precursor, and nitric acid (65% solution, Merck) was employed as acid catalyst to promote the formation of polymeric sols. A given amount of a water/nitric acid solution was dissolved in a large volume of alcohol to keep the local concentration of water low. The resulting solution was added under vigorous stirring to a titanium alkoxide/alcohol solution. All experiments were performed in a dry nitrogen atmosphere to avoid possible reactions of the alkoxides with water vapor from ambient air.

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Titania top layers were deposited by dip-coating technique on mesoporous γ-alumina [15] or anatase titania [16] coated α-alumina substrates [17]. To avoid the effect of strong capillary forces drying was performed in an alcohol-saturated atmosphere over a period of 48 h. The dried membranes were calcined in air at 300°C for 3 h. Unsupported material was prepared by drying of the sol in air and subsequent calcination under similar conditions as supported layers.

The particle sizes of the sols were measured by a ZetaSizer (Malvern, UK). The lower limit for accurate detection as specified by the manufacturer is around 2 nm. Therefore, when values below 2 nm are mentioned in the text below, they should be considered as an indication rather than as an absolute value. The thermal and phase evolution of dried uncalcined powder was studied by temperature programmed X-ray diffraction experiments (Philips SR5056, Panalytical, Almelo, The Netherlands). The chemical stability of amorphous titania was determined at room temperature by static solubility tests [13] in water at pH 1–13 using calcined unsupported material. In all the cases, 1 g of powder was immersed in 50 ml of water solution. The pH of the solutions was adjusted with nitric acid or ammonium hydroxide and the total weight loss of the powder after 120 h immersion was calculated by measuring the concentration of dissolved titania in the solution using atomic adsorption spectroscopy (Thermo-Optec BV SOLAAR system 939). The material was regarded as stable when the amount of dissolved titania in the solution was lower than or close to the AAS detection limit of 0.1 mg/l for titanium. The thickness and quality of the layers was checked with HR-SEM (LEO Gemini 1550 FEG-SEM, UK), permporometry [18] and liquid permeation experiments [19]. The water permeability of the membranes was measured in a pressurized dead-end filtration cell [19]. The determination of flux was conducted with fully desalinated, pre-filtered water. The retention of polyethylene glycol (PEG) was measured in order to determine the molecular weight cut-off. An aqueous solution of PEG with a molecular weight of 200 g/mol was filtered by the membrane under a pressure of 12 bar.

3. Results and Discussion

The procedure for polymeric titania sol synthesis was optimized. It was found that low molecular weight polymeric sols could be obtained only when the hydrolysis conditions were strictly controlled. For a given
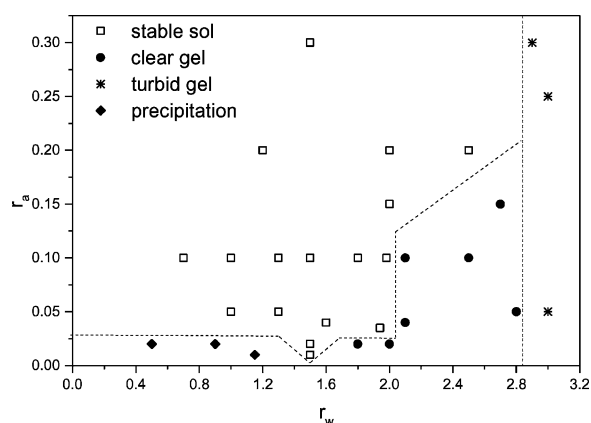

Figure 1. Influence of hydrolysis and inhibition ratios on sol state.

titanium concentration, the hydrolysis-condensation reactions were mainly governed by two parameters, namely the initial hydrolysis ratio $r_w = [H_2O]/[Ti]$ and the inhibitor ratio $r_a = [H^+]/[Ti]$. The hydrolysis of titanium-tetra-ethoxide in the presence of different amounts of acid and water led to sols, turbid or clear gels, or precipitates, depending on r_w and r_a, as shown in Fig. 1. It was found that a pH of at least 3 was required to form polymeric sols. At higher acid concentrations, H^+ favored the hydrolysis reaction by making the alkoxy ligands better leaving groups [2]. However, the main affecting parameter for the particle size was found to be the hydrolysis ratio, which had to be kept at values below 2 to prevent fast gelation of the sol. The average particle size (24 h after synthesis) varied between 1.6 and 3.7 nm, depending on the water to titanium ratio (see Table 1). Larger ratios gave rise to larger particles, but also to larger BET surface areas, indicating the optimal amount of water used for the reaction.

Table 1. Average particle sizes in the sol, and BET surface area of TiO_2 calcined at 300°C as function of the water to titanium ratio. Inhibition ratio (r_a) was fixed at 1.5.

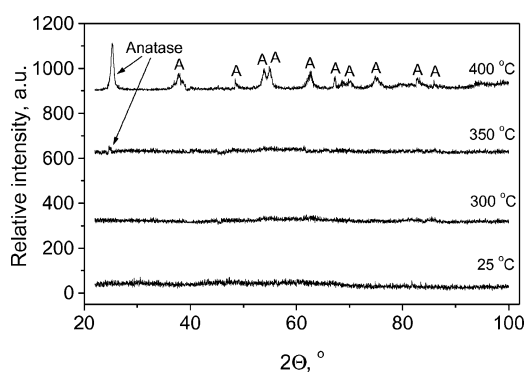| $r_w = [H_2O]/[Ti]$	Particle size (nm)	BET surface area (m²/g)
0.7	1.6	138.3
1.0	1.7	133.7
1.3	3.1	165.5
1.5	3.4	171.2
1.7	3.6	193.5
1.9	3.7	195.7
2.1	GEL	n.m.

Figure 2. Temperature programmed XRD spectra of amorphous titania at different temperatures.

Upon aging of the sols no significant increase of the particle size was seen, except during the first 24 h, which is therefore considered to be the period needed for sol stabilization.

Dried ethanol was used as solvent in all cases. High dilution ratios (<2 M Ti, and <5 M H_2O in alcohol) were found to be crucial to obtain small particles, but also to avoid precipitation in some cases. In addition, the duration and temperature of peptization were found to influence the results significantly. Stable sols with small particle sizes were obtained when refluxing was carried out at 60°C for 10 min.

Temperature programmed XRD spectra are shown in Fig. 2. It can be seen that the material retains its amorphous structure until 300–350°C, while at 400°C a (partial) phase transformation into the crystalline anatase phase occurred. Results from the chemical stability tests indicated that amorphous titania is stable in the pH interval 2–13. At lower pH significant weight losses were found.

Highly reproducible, homogeneous and crack-free amorphous titania layers were obtained on both mesoporous substrates, as shown in Fig. 3. It was found that the layer thickness could be varied in the range 40–200 nm by changing the sol concentration prior to deposition of the layer. Figure 4 shows the volumetric water flux at steady state. A linear dependency between flux and pressure applied over the membrane is observed, which indicates that the pressure difference is the only driving force for permeation. For transport only driven by convection the volume flow rate (F) is directly proportional to the pressure difference (ΔP):

$$F = B^o \Delta P,$$

where B^o is the total (pseudo) permeability.

However, relatively low fluxes of 3–6 dm^3/m^2 h were achieved in the pressure range of 9–16 bar. The same graph also shows results obtained on a macroporous α-alumina support (pore size $\sim$100 nm [17]) and an α-alumina supported mesoporous γ-alumina nanofiltration membrane (pore size $\sim$5.0 nm, layer thickness
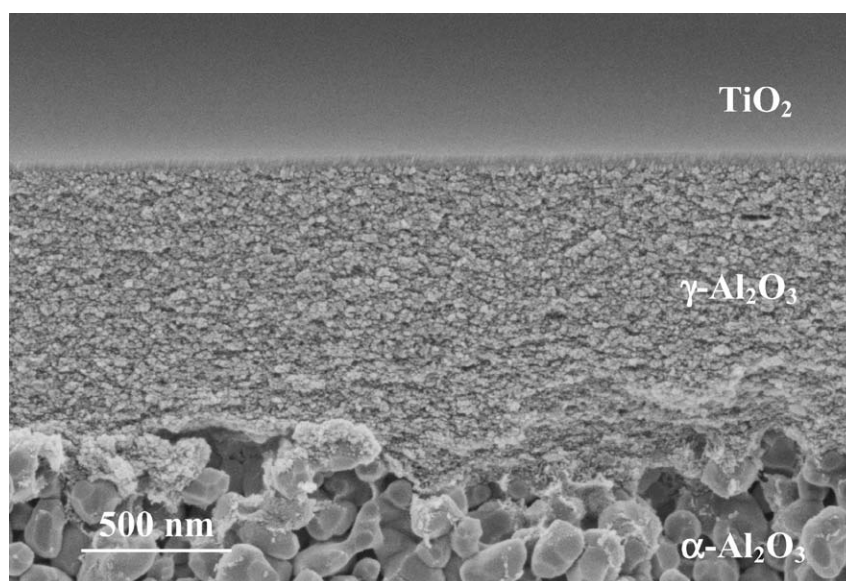

Figure 3. SEM picture of cross section of amorphous TiO_2 layer on γ-Al_2O_3 coated α-Al_2O_3 substrate.
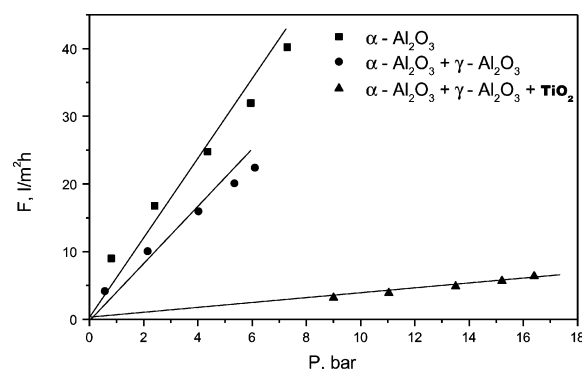
Figure 4. Water fluxes through different membranes versus applied pressure.

$\sim$3 μm [15, 19]) for the sake of comparison. The retention of PEG ($M_w = 200$ g/mol) was nearly 100%. This value corresponds to an average pore diameter of $\sim$0.8 nm according to the Stokes-Einstein radius model [11]. Considering these excellent retention properties, this membrane may be very suitable for specific nanofiltration applications where retention rather than permeability is of importance.

4. Conclusions

Highly reproducible amorphous microporous titania layers with pore size $\leq$0.8 nm were obtained on both mesoporous γ-alumina and titania/zirconia coated substrates. The upper limit of thermal stability of the amorphous phase is $\sim$300°C. At higher temperatures led to the crystallization of the material into anatase, which is accompanied by a collapse of the microstructure. Moreover, a high chemical stability was achieved. A retention of nearly 100% for PEG with $M_w = 200$ g/mol was measured.

Acknowledgment

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