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Textural stability of yttria-doped titania membranes

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The textural stability of yttria-doped titania membranes prepared by the sol-gel method was studied using thermal analysis, X-ray diffraction (XRD), Raman spectroscopy, scanning electron microscopy (SEM), and N_2 physisorption techniques. In the membrane fabrication process, the hydrolysis time and geometry of the substituent group in the metal alkoxide precursor directly affected the particle size of the sol. An improvement in thermal stability was achieved in the 3 mol% yttria-doped titania membranes resulting in the retardation of the anatase-to-rutile phase transformation in the doped samples. This technology has potential application in preventing membrane cracking at high temperatures. XRD results revealed that pure and yttria-doped titanias transformed to more than 90% of rutile at temperatures higher than 600 and 800°C, respectively.

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1. Introduction

Polymeric membranes have been commercially available for many years and are employed in large-scale operations [1] as they offer significant flexibility and respond to a wide range of process requirements. However, organic solvents, dry atmospheres, and high temperatures may cause these materials to deteriorate and lose permeability. Since hydrolysis of the membrane materials may occur for a wide range of pH values, the membranes are quite sensitive to enzymes and microorganisms. These unfavorable environments can be overcome by making membranes that are thermally and chemically more stable. Inorganic membranes are one example of such and can be used for a wide range of applications.

The applications of inorganic membranes have recently been reviewed [2, 3]. The thermal stability of these materials allows them to be potential catalysts in high-temperature membrane reactors. Although the basic idea is already known, an evaluation of this concept in terms of a number of aspects has just been published [4–6]. However, there is still a lack of information concerning the textural stability of these membranes.

In order to evaluate the efficiency of inorganic membranes for high-temperature applications, a thermally stable membrane is required containing uniform small-sized pores supported on porous ceramic materials. The pore size of a titania membrane prepared using the sol-gel method in this work was found to be in the range of 3–5 nm.

At a relatively high temperature (~450°C), the pores in the top layers of a titania membrane are small and their distribution is narrow. Phase transformation from anatase to rutile occurs above this temperature [7] and results in an 8% volume change. This change introduces extra stress during sintering and causes a collapse in the membrane structure. In constructing these top layers, a uniform colloidal $Ti(OH)_4$ suspension was chosen as the coating material. The addition of a binder, such as hydroxypropylcellose (HPC) and polyvinylalcohol (PVA), has been proven to enhance the formation of a crack-free texture and minimize the stress developed during drying [8]. The structural transformation is related to the size and shape of the titania sol particle [9]. Temperature treatment also has an important effect on the quality of the membrane.

In a titania membrane, the main mechanism involved in reducing the porosity and the surface area is the enhanced sintering during the anatase-to-rutile phase transformation. Below 500°C, the reductions in the porosity and the surface area due to the growth of the anatase crystallites, and hydrothermal sintering are small compared with those caused by the enhanced densification from the anatase-to-rutile phase transformation. The decrease of porosity in a titania membrane can be suppressed by slowing down the growth rate of the anatase crystallites before the phase transformation, or by retarding this phase transformation to a higher temperature. It is known [10] that the presence of a second oxide, such as alumina or lanthana, in the titania sol

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can decrease the rate of grain growth during the initial stage of sintering and thus retard the anatase-to-rutile phase transformation. In this work, we investigated the stability and the effect of heat treatment on the nanostructure of a membrane. We believe we have created a new method for the improved synthesis of crack-free titania membranes with small pore sizes arising from ultra-fine particles. The doping of yttria in titania membranes was designed to suppress the crystallite growth and retard the phase transformation, thereby improving the textural properties and thermal stability of these materials.

2. Experimental

A conventional way of preparing a multi-component oxide membrane is to mix alkoxides of the desired product or components with the dopant-containing salts in the solvent during the sol stage. After deposition, dehydration and dealcoholization of the gel, and decomposition of the dopant salt in the calcination step, a membrane is formed.

Titania sols were prepared by the hydrolysis of titanium butoxide at room temperature. A volume of 400 ml of water per mole of alkoxide was used for hydrolysis. A certain amount of titanium butoxide was added dropwise to the water at a high rate of stirring. Then the resultant white precipitate of titanium hydroxide was peptized with nitric acid at a 0.5 H^+/Ti^{4+} molar ratio. Peptization with refluxing was allowed to proceed overnight at a temperature above 80°C. The final product obtained was a clear blue stable titania sol [11].

A 10 wt% PVA solution was prepared with the PVA obtained from Fluka (MW = 72000). Twenty milliliters of this solution was added to 100 ml of sol solution. After 2 h stirring and 1 h setting, the sol was ready to be used for coating. The PVA acted as a binder to prevent crack forming during the drying process.

In this work, yttria was doped in the titania membranes using the solution-sol mixing method. A 0.25 M yttrium nitrate solution was prepared with the yttrium nitrate obtained from Acros. Thirty milliliters of this solution and 20 ml of the PVA solution were thoroughly mixed into a controlled amount of a titania sol so that the membrane would contain 3 mol% of yttria and 10 wt% PVA. In doping the yttrium nitrate in the titania sols, the pH value of the mixed sol was kept constant so that the stability and particle size of the doped sol remained unaffected. Since the isoelectric point of the titania sol was reported to be in the range of 5–6 [12], the pH values of the titania sols, both pure and doped, were kept below 3. To investigate the improvement of the thermal stability in the titania membranes, samples of the pure and doped titania membranes were heat-treated under the same conditions.

Supported membranes were coated on porous supports (40–45% porosity and a mean pore size of 200 nm) by dipping a ceramic support tube into the sol in a single dipping process for 10 seconds. All samples were dried at 40°C and 60% relative humidity (RH) until constant weights were obtained. The thicknesses of the supported and unsupported membranes after drying were ca. 6 and 15 μm, respectively. Further calcinations were carried out at 100 to 900°C for 2 h.

The sizes of the sol particles were determined by light scattering measurements (Coulter N4 Plus). The surface area, pore volume, and pore-size distribution of the unsupported membranes were characterized by N_2 ad(de)sorption isotherms using an adsorption porosimeter (Micromeritics NOVO 1000). Although the pore size and pore-size distribution in a thin layer could not be determined, the pinholes and surface cracks were indistinguishable from the macro- or mesopores. Moreover, by assuming that the pore-size distribution in a supported membrane might not deviate significantly from that of an unsupported one, evaluations of these properties were performed using unsupported samples. The phase structure of a titania membrane was determined by an X-ray diffractometer (D/MAX-3C) with Ni-filtered Cu K_α radiation at a 2θ scanning speed of $4^\circ\,\mathrm{min}^{-1}$. The voltage and current of the X-ray source were 30 kV and 20 mA, respectively. Raman spectroscopy was also used for characterization. To determine the anatase-to-rutile phase transformation, the XRD peaks of (101) anatase and (110) rutile were used to calculate the phase composition according to the equation [13]:

$$[\text{anatase}]/[\text{rutile}] = 0.79(I_{101}/I_{110}).$$

The thickness of the film was determined by SEM on the fractured surface of the membrane. Characterization of the thermal properties of these materials was achieved by differential thermal analysis (DTA) (Seiko). Samples of unsupported membranes were heat-treated at $10^\circ\mathrm{C/min}^{-1}$ and used for thermal analysis.

3. Results and discussion

In this work, a sol-gel method [14] was used to make inorganic membranes. When a particulate sol is employed to fabricate a membrane, the size of the pores is dictated by the size of the particles in the sol [15]. Hence, a sol containing ultra-fine particles is necessary in order to fabricate a membrane with pores of a very small size.

Preparation of a particulate sol includes hydrolysis and peptization processes. The particle size of the sol can be affected by the type and amount of acid employed as a peptizing agent [16], and also by the time in the hydrolysis process. The relative rate of the hydrolysis and peptization thus determines the size of the particles. If the rate of hydrolysis is faster than that of peptization, large-sized aggregates will be formed. In contrast, if the rate of hydrolysis is slower than that of peptization, fine particles will be obtained. Fig. 1 shows the distribution of particle sizes in a pure titania sol at different hydrolysis times. "0 min" of hydrolysis time means that hydrolysis and peptization occur simultaneously. This "0 minute" time yields the narrowest distribution. In practice [17], filtering and washing have to be carried out as quickly as possible in order to prevent aggregation of the precipitates in the sol. In this work, the hydrolysis time was controlled

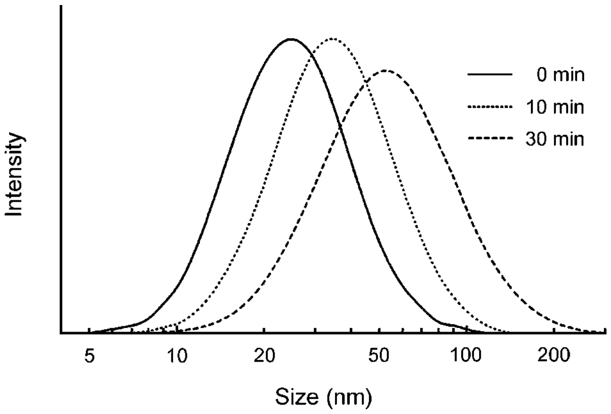

Figure 1 Effect of hydrolysis time on the particle size distribution in pure titania sols.

to the lowest time limit so that aggregation could be avoided.

The kinetics of hydrolysis can be controlled by altering the properties of the reactants. For example, the rate of hydrolysis can be reduced by using a higher branching substituent group in the metal alkoxide. The rate of hydrolysis was reduced from 24 nm to 20 nm by replacing the n-butoxide group with an isopropoxide group. As the hydrolysis step is more sterically hindered by the isopropoxide moiety, the reaction rate decreases slowly enough to allow the fresh precipitates to be peptized to form finer particles. Yu [15] obtained a large branched alkoxyl group in metal tetra-tert-amyloxide by reacting metal propoxide (isopropoxide in the case of titanium and normal propoxide for zirconium) with tert-amyl alcohol (t-AmOH) in benzene solvent. By using this large group as a precursor, sols with a particle size of less than 3 nm were prepared.

DTA was performed on the pure and yttria-doped titania gels dried at 110°C. The results are shown in Fig. 2. In both gels, the weak peaks at 250°C are due to the combustion of the organic substances contained in the gels [18]. The broad peaks in both samples from 400 to 800°C are attributed to crystallization. Although they cannot be fully resolved for the pure titania gel, there are two mixture points clearly shown at 480 and 550°C. These are due to the formation of the anatase and rutile phases, respectively. For the yttria-doped gel, the peak at 550°C is missing in this temperature range. This suggests that the rutile phase in the yttria-doped gel occurs at a higher temperature.

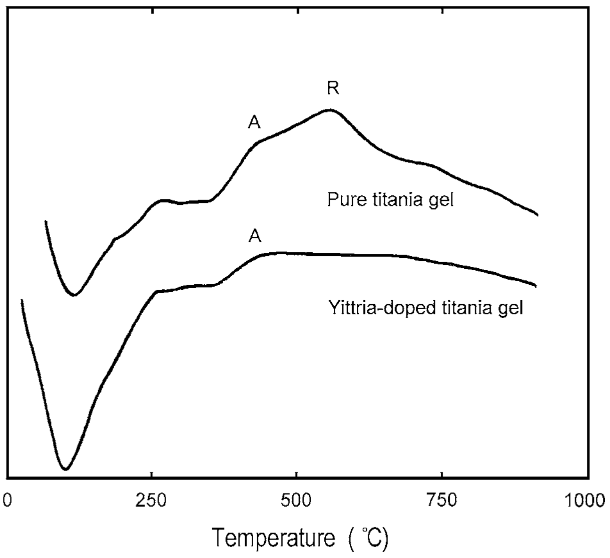

Figure 2 The DTA curves of a pure titania gel and an yttria-doped titania gel (*A* = anatase titania, *R* = rutile titania).

The XRD patterns of the pure titania membranes calcined for 2 h at different temperatures are shown in Fig. 3. The peaks marked *A* and *R* represent the anatase and rutile phases, respectively. Those having the strongest peaks [19] of anatase and rutile are located at $2\theta = 25.6°$ (101) and 27.4° (110), respectively. The dried gel mainly contains embryo crystals of anatase. Broad crystalline peaks grow with increasing temperature until reaching 400°C, where the peaks of the anatase are clearly resolved. For the pure titania membrane, calcination at 400°C not only consolidates the titania gel but also facilitates the phase transformation in titania from the amorphous phase to the anatase and rutile phases. The XRD pattern of the pure titania sample heat-treated to 600°C indicates that the transformation to the rutile phase is complete. Fig. 4 shows the XRD patterns of the yttria-doped titania membranes calcined at various temperatures. Below 600°C, anatase is mainly present and the peaks are very broad. At 700°C, some new peaks corresponding to rutile start to appear. By 800°C, more than 90% rutile is formed. As mentioned before, no sharp transformation temperature appears in the DTA results. For 90% of the

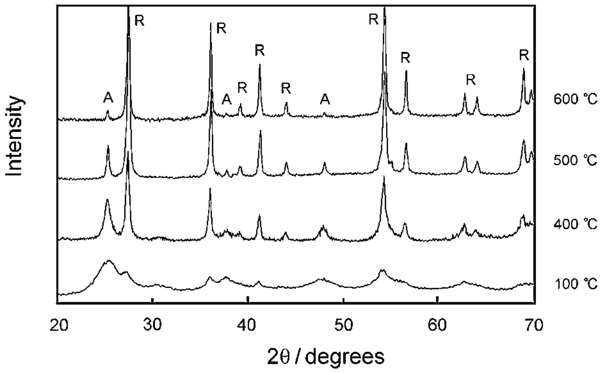

Figure 3 The XRD patterns of pure titania membranes heat-treated at different temperatures (*A* = anatase titania, *R* = rutile titania).

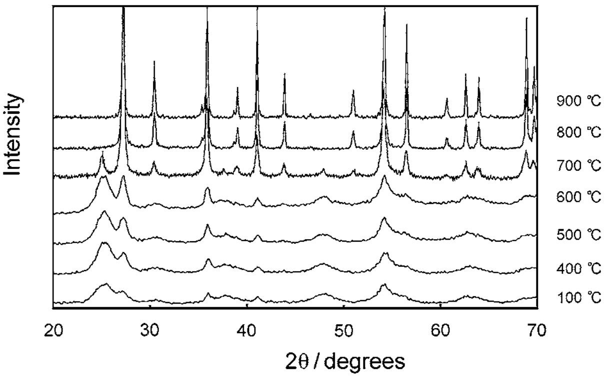

Figure 4 The XRD patterns of yttria-doped titania membranes heat-treated at different temperatures.

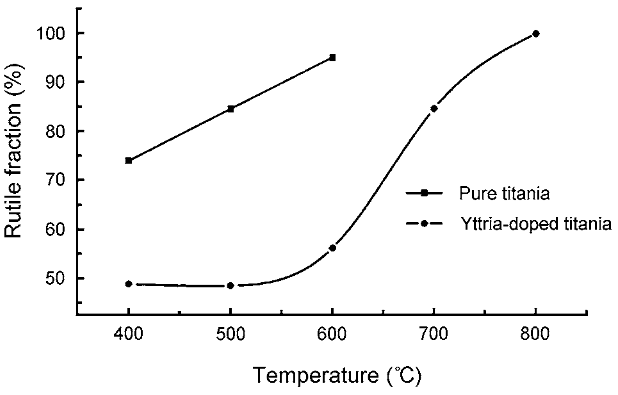

Figure 5 The comparison of the rutile fraction between pure and doped titania at different temperatures.

anatase-to-rutile transformation in pure titania membranes, the temperature is 600°C, while it is ca. 200°C higher in the yttria-doped samples. This suggests that the yttria doping using the sol-gel method retards the anatase-to-rutile transformation and has no effect on the transformation from the amorphous phase to the anatase phase.

The rutile fractions calculated from the intensities of I_{110}(rutile) and I_{101}(anatase) for pure and yttria-doped titania samples at different temperatures are shown in Fig. 5. For pure titania, the rutile fraction increases rapidly after 400°C, while for yttria-doped titania, the phase transformation is retarded to 600°C.

The Raman spectra of the pure and yttria-doped titania membranes heat-treated at different temperatures are shown in Figs 6 and 7. The anatase phase appears at 143, 195, 395, 513, and 638 cm^{-1}, which corresponds with the reported frequencies [20] of anatase in single crystals.

The common feature of these spectra is the presence of broad peaks at 447 and 608 cm^{-1}, which were assigned to the rutile phase of titania. The most characteristic difference among these spectra is the change in intensity of the 150 cm^{-1} line relative to the 447 and 608 cm^{-1} lines. The 150 cm^{-1} line, which is the shifted 143 cm^{-1} line, is the most intense line of the anatase phase and is an index for determining the relative amount of anatase and rutile by comparing the 608 cm^{-1} line of rutile.

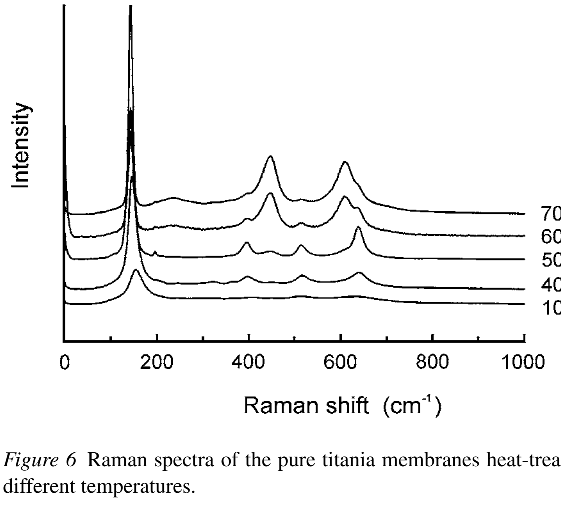

Figure 6 Raman spectra of the pure titania membranes heat-treated at different temperatures.

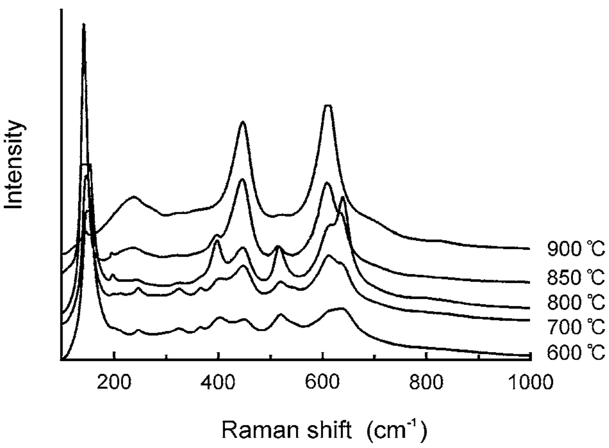

Figure 7 Raman spectra of the yttria-doped titania membranes heat-treated at different temperatures.

Figs 6 and 7 also show a coarsening in the anatase phase (142–154 cm^{-1}) form of embryo crystals upon heat treatment on both pure and yttria-doped gels. It was found that the size of the microcrystals increased with the temperature as the width (FWHM) of the 150 cm^{-1} peak appeared narrower at a higher temperature. The FWHM of this peak decreases from about 39 cm^{-1} to 11 cm^{-1} in the samples heat-treated at 100 and 400°C, respectively. It is important to note that all the anatase peaks are red-sifted at a higher temperature. The 152 cm^{-1} peak shifts to 142 cm^{-1}, the 246 to 237, the 449 to 448, and the 612 to 611. The shifts are due to oxygen deficiency in the high-temperature phases of the material [21].

Upon heat treatment at 700°C for 2 h, the growth of the rutile phase was observed both by XRD and Raman spectrum. As mentioned before, doped yttria can retard the anatase-to-rutile transformation. Our results for the yttria-doped titania membranes indicate that the transformation to the rutile phase is mostly completed at 850°C, and the Raman spectrum reproduces the literature data of rutile (peaks at 143, 448, and 611 cm^{-1}, and a strong combination band at 239 cm^{-1}). Further heat treatments at temperatures higher than 900°C produce no further change in the XRD and the Raman spectrum.

4. Conclusions

The 3 mol% yttria-doped titania membranes fabricated using the sol-gel method exhibit significant improvement in thermal stability compared with the pure titania membranes.

Sols of a small particle size in the ca. 20 nm diameter range were prepared using metal alkoxide containing higher branching isopropoxide groups, which replaced the conventional n-butoxide group.

The anatase-to-rutile phase transformation temperature in the yttria-doped titania is 200°C higher than that in pure titania. This suggests that the yttria-doping technique has potential application in preventing cracking in membranes recognized to operate at elevated temperatures.

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