

Thermal stability of TiY membrane

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Three mol % yttria-doped titania membranes were prepared by the sol-gel method. Their pore and phase structures were determined by N₂ sorption and X-ray diffraction. It was shown that these membranes had superior properties over the undoped membranes in having higher thermal stability. In practice, yttria doping can be developed for high temperature applications. © 1999 Kluwer Academic Publishers

1. Introduction

Inorganic membranes have potential applications in high temperature catalytic reactions and gas separations [1, 2]. In high temperature applications, the membrane is used as support on which a gas separation layer or catalyst layer is coated. With a technical matching to the manufacturer's specification, these inorganic membranes may be employed for hot gas filtration [3]. Thus, thermal stability of these membranes is an important concern.

A membrane being thermally stable means that the properties of the membrane remain unchanged or changed negligibly at a specific temperature. Titania membranes with pore size in the range of 3–5 nm were prepared using the sol-gel method [4–6]. However, only a few studies on the thermal stability of titania membranes have been published.

It was found [7] that phase transformation (anatase to rutile) of titania membrane occurs at about 400 °C. At this temperature, phase transformation leads to significant change in the pore structure of the membrane due to the formation of large crystals in the new phase. Furthermore, since this new phase has a different lattice structure and volume, phase transformation usually creates cracks. Therefore, phase transformation in a titania membrane must be avoided during the preparation processes and when in use. We have reported that phase transformation temperature was affected by the different preparation method for titania particle sol [8].

Lin *et al.* [9] found that phase transformation of an inorganic membrane proceeded via nucleation on the grain surface or boundary and crystal growth. The phase transformation rate is proportional to the number of nucleation sites and the activation energy of nucleation. Retardation of the phase transformation of a metal oxide (the first oxide) can be achieved by doping a second oxide onto it if the dopant covers its grain surface. This reduces the grain boundary nucleation sites and increases the activation energy of nucleation [10].

In this work, an yttria-doped technique was employed to improve the thermal stability of the titania membranes prepared by the sol-gel method. Yttria causes retardation in phase transformation and sintering in titania membranes. The main objective of this paper is to report a comparative study on the improvement of thermal stability in yttria doped titania membranes in an unsupported form. Yttria was chosen as the second oxide because the radius (1.04 Å) of Y³⁺ was larger than that of the Ti⁴⁺ (0.81 Å). It was found [11] that formation of a monolayer of the second oxide on the surface of the first oxide particles was a thermodynamically favorable process if the second oxide had a larger metal ion size than that of the first oxide and could form strong bonds with the first oxide particles [12].

2. Experimental

Titanium isopropoxide (Aldrich) was used as starting material in preparing the titania sol. Titanium isopropoxide (TIP) was added dropwise to an aqueous solution of nitric acid (0.01N). The resultant Ti⁴⁺ concentration was about 0.3 mol dm⁻³ and the H⁺/Ti⁴⁺ mole ratio was 0.5 in solution. The reaction was carried out with stirring at room temperature for about 30 min and was subsequently further peptized at above 80 °C for about 1 hour. A white precipitate of titanium hydroxide was peptized with nitric acid to produce a clear blue stable titania sol [8], which was then mixed with the yttrium chloride solution in a specific composition at a controlled pH value of 3. This yttrium-doped sol was poured into a petri dish to form xerogel by drying at room temperature and under 60% relative humidity followed by calcining. A supported membrane was formed by dipping a dry support into the sol. The capillary pressure drop created by the pores of the support thus forced the dispersion medium into the support, while the particles were concentrated at the surface and gelation occurred. The coated support was dried over

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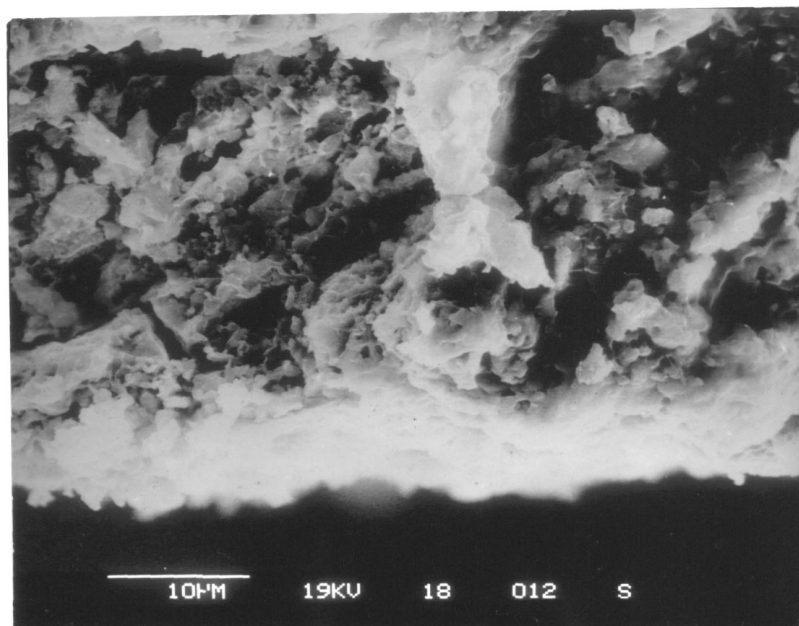


Figure 1 The SEM picture of a cross-section of support membrane.

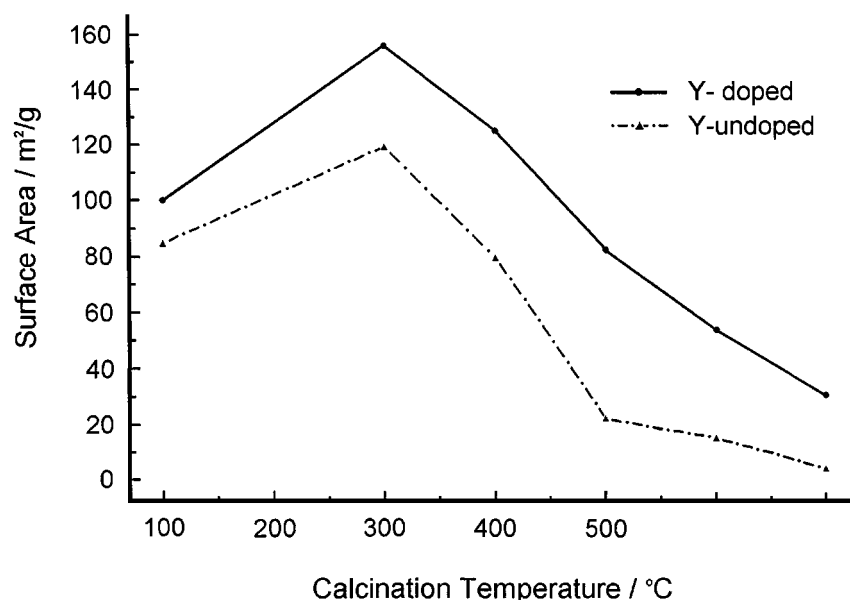


Figure 2 Comparison of the effect of heat treatment temperature on the surface area of the yttria-doped titania membrane and that of the undoped titania membrane.

night at room temperature and 60% relative humidity, followed by calcination at a desired temperature for 5 h. This process was repeated to reach a certain thickness in the membrane. A SEM picture of a cross-section of a supported membrane is shown in Fig. 1.

In doping the yttrium chloride into the titania sol, the pH value of the mixed sol was kept unchanged so that the doped sol was stable with a negligible change in particle size.

The porous structures of titania membranes were characterized by nitrogen adsorption (ASAP 2000). The specific surface area was calculated from the BET equation. The phase structures of the titania membranes were identified by an X-ray diffractometer (D/MAX-3C).

3. Results and discussion

Figs 2 and 3 show the comparison of the effect of heat treatment temperature on the surface area and average pore size of the yttria doped titania membranes with those of the corresponding undoped membranes. In all cases, the doped membranes have larger surface areas and slightly smaller pore sizes than those of the undoped ones.

Fig. 2 shows that the trend of change in surface area of the yttria-doped and undoped membranes are similar in line shapes. When the heat treatment temperature was below 300 °C, the surface area increased with increasing temperature. At such temperatures the gel was considered in a process of further dehydration. The primary sol particles were consolidated to form an embryonic

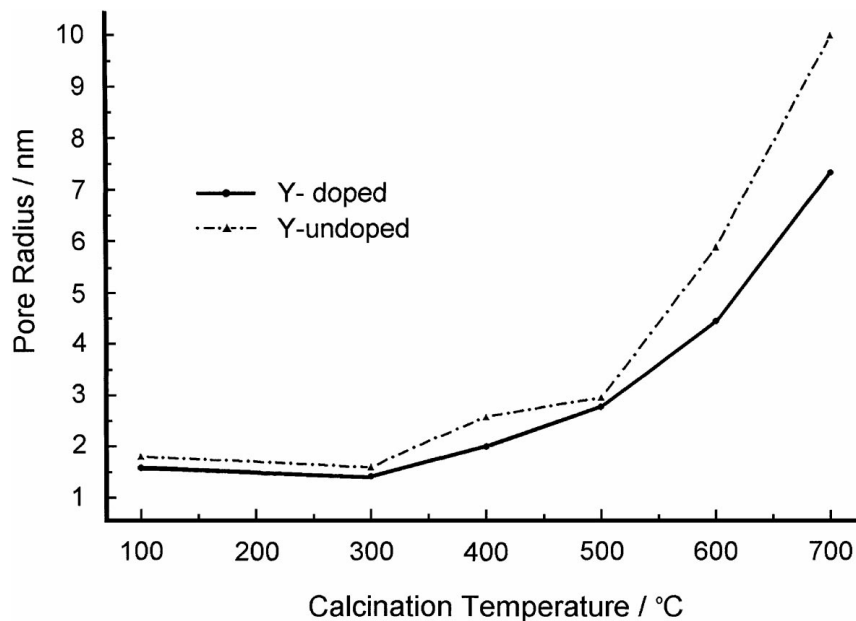


Figure 3 Comparison of the effect of heat treatment temperature on the pore size of the yttria-doped titania membrane and that of the undoped titania membrane.

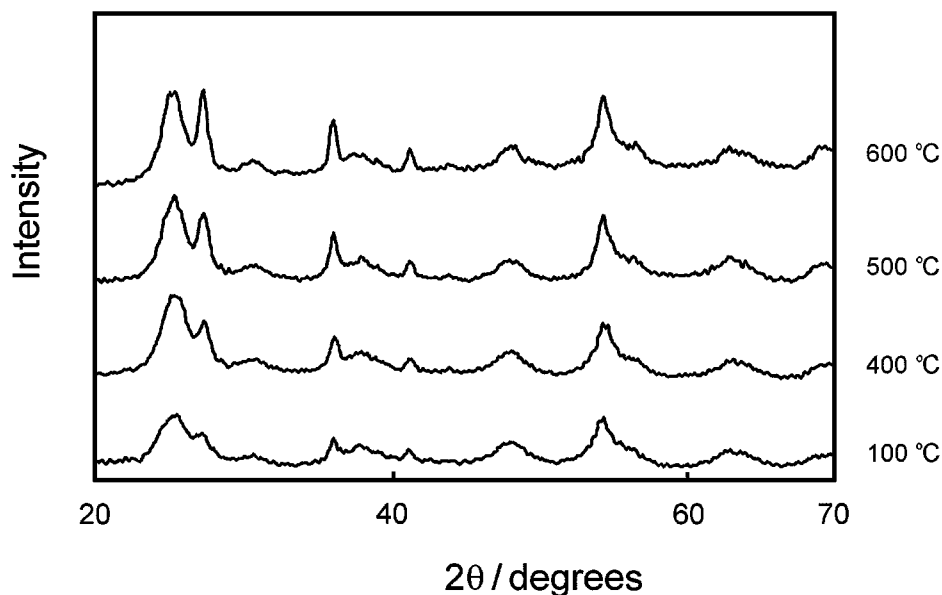


Figure 4 XRD spectra of the yttria-doped titania membrane after heat treatments at different temperatures.

crystal during drying [13]. At most calcination temperatures above 300 °C, the surface area of a doped membrane was about 50 m²/g which was larger than that of the undoped one. On the other hand, the differences in pore size of the membranes were not significant except at 600 °C as shown in Fig. 3.

The slight difference in pore size of the oxide-doped ceramic membrane from the undoped one is likely due to the changes of size and shape of the primary particles after doping. The introduction of the Y³⁺ ions in titania sol may have altered the charge distribution around the sol particles slightly, and this affects the shape and size of the primary particles. Nevertheless, this deviation is small from a practical viewpoint. Our results show that the doping method has a negligible effect on the sol stability and the pore structure of the membranes. The XRD patterns of the yttria-doped tita-

nia membranes and the corresponding undoped ones at different calcination temperatures are shown in Figs 4 and 5.

As shown in Fig. 4, the XRD spectra of the yttria-doped titania membrane after calcination do not exhibit clear peaks of the rutile phase. The anatase peaks, although observable, are very broad. It appears that the doped titania membrane comprises a certain amount of amorphous titania, but mainly anatase crystals at temperatures below 600 °C. The crystallite size of the titania can be calculated with the Scherrer equation [14]. For the doped titania membrane, the XRD results given in Fig. 3 indicate that the heat treatment at different temperatures does not completely convert the amorphous titania to anatase. It is believed that yttria doping also retards crystal phase formation in titania from amorphous to tetragonal.

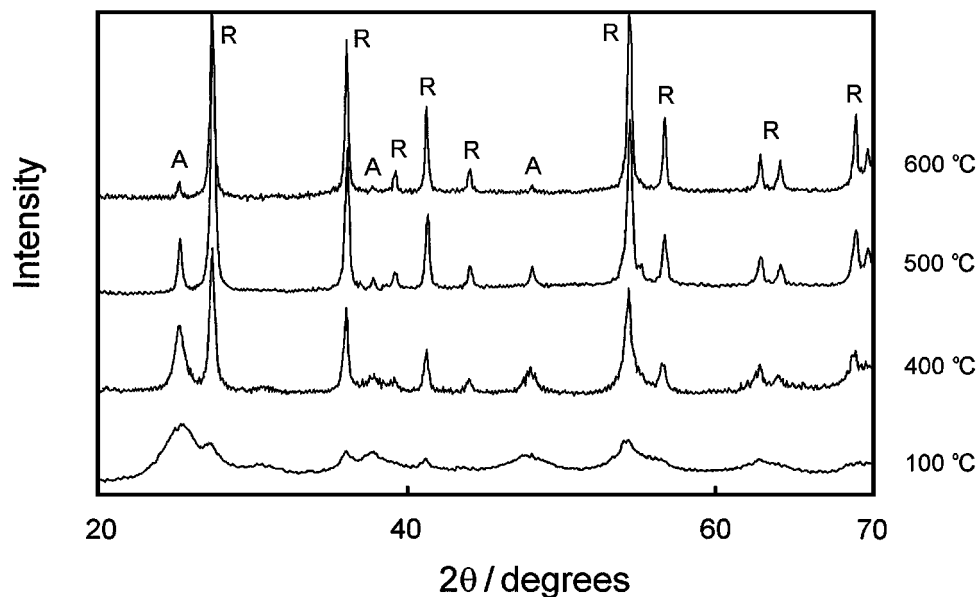


Figure 5 XRD spectra of the titania membrane without yttria after heat treatments at different temperatures (R = rutile titania, A = anatase titania).

The phase transformation temperature of the yttria-doped membrane is at least 200 °C higher than that of the pure titania membrane. So yttria doping can retard the phase transformation.

Since sintering of an inorganic membrane is governed by the surface diffusion mechanism, the sintering rate decreases as the specific grain surface energy decreases. Covering the grain surface with yttria may lower the specific surface energy of titania and the activation energy of diffusion, thus reducing the sintering rate.

Titania xerogel, after drying, is in an amorphous form. For the undoped titania membrane, the calcination step (400 °C for 1 h) not only has consolidated the titania gel but also has facilitated the phase transformation from amorphous to anatase and rutile. Fig. 5 shows the XRD spectra of an undoped titania membrane. From the calculation [15], the fraction of rutile should reach 70 wt % at 400 °C and 92 wt % at 600 °C.

4. Conclusion

The yttria-doped titania membrane has been shown to have higher thermal stability than the undoped one. Although this membrane exhibits similar trend of change in surface area with respect to heat treatment, its surface area is typically about 50 m²/g larger than that of an undoped one, and its phase transformation temperature can be retarded at least to 200 °C. The process of doping yttria in an inorganic membrane could thus be useful in high temperature applications.

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