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# Hydrothermal stability of pure and modified microporous silica membranes

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The hydrothermal stability of microporous (0.6 nm) silica membranes prepared by the sol–gel process was studied at 600 and 800 °C in a 50 mol% steam atmosphere. The membranes remained microporous after calcination and hydrothermal treatment at 600 °C for 30 h but a substantial reduction in the specific surface area (48%) accompanied by a 77% decline in the micropore volume was observed. Hydrothermal treatment at 800 °C for 30 h resulted in complete densification of the membranes. The effect of alumina and magnesia on the hydrothermal stability of the membranes was investigated. Both $Al_2O_3$ and MgO were introduced into the membranes by doping the starting silica sol with controlled amounts of the corresponding nitrate salts. Alumina did not change the pore structure of the silica membranes which retained a large part of their microporosity after hydrothermal treatment at 600 °C compared to pure silica membranes. Doping with magnesia, however, resulted in lower specific surface areas relative to those of pure and alumina-doped silica membranes after drying and calcination. These effects on the stability of the membranes are explained by assuming structural changes in the membranes catalysed by magnesia.

## 1. Introduction

Inorganic membranes have attracted great attention recently for their high chemical, thermal and mechanical stability [1]. These characteristics are important in applications involving high temperatures and acids. Among all ceramic membranes that have been studied so far, microporous silica membranes have shown high permselectivities for hydrogen and methane with an activated permeation mechanism [2]. The term microporous refers to materials with a pore diameter smaller than 2 nm [3].

Microporous silica membranes have been prepared both by the sol–gel and the chemical vapour deposition (CVD) process. A modified CVD process was used to develop dense silica membranes within the walls of porous Vycor glass tubes by oxidation of $SiH_4$ or hydrolysis of $SiCl_4$ [4–6]. These membranes were highly selective to hydrogen permeation but suffered from densification at temperatures above 600 °C. In the presence of steam, the densification was more severe and the hydrogen permeability was substantially reduced. A modification of this process involving the reaction of tri-isopropylsilane with oxygen within the pores of Vycor glass substrates resulted in $SiO_2/C$ deposits that were thermally stable up to 800 °C [7]. Hydrogen-permselective silica films were also deposited within the pores of porous glass supports by thermal decomposition of tetraethylorthosilicate (TEOS) [8, 9].

The sol–gel process was used to coat fibrous mats with microporous silica layers to improve the filtration efficiency [10]. The effect of preparation parameters on the quality of the obtained membranes in this particular application was also studied [11]. It was found that low catalyst concentrations resulted in microporosity. Unsupported microporous silica membranes were recently prepared by hydrolysis and condensation of TEOS to study the effect of synthesis conditions on the physical properties of the membranes [2].

Microporous thin layers of sol–gel derived silica have also been used to modify and improve the separation characteristics of other ceramic membranes. Uhlhorn *et al.* [12] prepared composite γ-alumina/silica membranes carrying a top layer of silica. This thin (thickness 30–60 nm) microporous layer resulted in improved selectivities for several gases at various temperatures and moderate pressure [2, 12]. $SiO_2$–$Al_2O_3$ and $SiO_2$–$TiO_2$ microporous films of improved chemical and thermal stability compared to pure silica were also deposited on γ-alumina membranes [13, 14]. Combinations of the CVD and the sol–gel process have also been used for preparing porous silica films [15].

It is known that microporous silica materials are not hydrothermally stable. Prolonged exposure of these materials to humid air at temperatures higher than the calcination temperature of silica (400 °C) causes rapid densification. These pore structure changes result in reduced selectivities and permeabilities of microporous membranes made of silica for hydrogen and methane [2, 4]. The hydrothermal stability of

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silica has not yet been systematically studied. The exact mechanism through which steam influences the sintering of silica is also not well understood at the present time. It has been proposed that steam catalyses the surface diffusion of silica which moves along the surface of larger pores to fill in pores of smaller dimensions [16, 17]. The hydrothermal stability problem is also encountered to a lesser extent in other ceramic membranes. Recently, the thermal and hydrothermal stability of alumina, titania and zirconia membranes prepared by sol–gel techniques was studied [18]. It was found that the effect of sintering on the pore structure of these membranes decreased in the order zirconia > titania > alumina. The stability of these membranes in the presence or absence of steam was improved by doping the alumina and titania membranes with lanthana and the zirconia membranes with yttria [19]. It has been shown in several studies that dopants can drastically alter the characteristics of ceramics. For example, Akhtar *et al.* [20, 21] found that the specific surface area of $TiO_2$ was increased by doping with $SiO_2$ while it was decreased by doping with $Al_2O_3$.

Understanding and improving the hydrothermal stability of microporous $SiO_2$ membranes are important to the practical application of these membranes in high-temperature gas separations and catalytic reactions. In this work, the hydrothermal stability of unsupported microporous silica membranes prepared by the sol–gel process was investigated. The pore-structure evolution during hydrothermal treatment was studied. The influence of $Al_2O_3$ and MgO dopants on the hydrothermal stability of the membranes was examined.

## 2. Experimental procedure

### 2.1. Materials

TEOS (Aldrich, 98%) was the precursor for the silica sol, ethanol (Midwest Grain Products Co.) was the solvent, and nitric acid (MCB reagents) was the catalyst. Aluminium nitrate nona-hydrate, $Al(NO_3)_3 \cdot 9H_2O$ (Fisher), and magnesium nitrate hexa-hydrate, $MgNO_3 \cdot 6H_2O$ (Fisher), were the salts used for doping the silica sol with $Al_2O_3$ and MgO, respectively. Distilled water was used for hydrolysis of TEOS.

### 2.2. Procedure

The silica sols were prepared by the acid-catalysed hydrolysis and condensation of TEOS [22]. The sol composition was 3.8 mol ethanol/mol TEOS, 6.5 mol water/mol TEOS and 0.09 mol nitric acid/mol TEOS. This sol composition was adopted from Uhlhorn *et al.* [2]. Solutions of TEOS/ethanol and nitric acid/water were prepared separately and mixed in a spherical flask equipped with a reflux condenser. The resulting sol was heated to 90 °C for 3 h and then cooled naturally to room temperature. Solutions of 10% wt/vol $Al(NO_3)_3 \cdot 9H_2O$ and 10% wt/vol $MgNO_3 \cdot 6H_2O$ in ethanol were prepared. Heating at moderate temperature for 15 min ensured complete dissolution of the salts in ethanol. Ethanol was chosen as the solvent for the salts because the same solvent was also used in the silica sol. Nitrate salts of aluminium and magnesium were employed because they are more compatible with the silica sol which was catalysed by nitric acid. Therefore, secondary effects by the introduction of the salts into the sol were minimized. On the other hand, $Al(NO_3)_3 \cdot 9H_2O$ is a common precursor that is used in the preparation of mullite and aluminosilicate gels [23, 24].

Doping the silica sol with $Al_2O_3$ or MgO was performed by mixing the sol with controlled amounts of the ethanol solutions of the salts. The salt metal to alkoxide metal (Al:Si and Mg:Si) weight ratios used were 3% and 6%. Dried membranes ( ~ 20 μm thick and 80 mm diameter) were prepared by placing the doped silica sols in plates and drying for 48 h in a controlled-humidity oven at 40 °C and at 60% relative humidity. Calcined membranes were obtained upon heating the unsupported dried films at 400 °C for 3 h in a temperature-programmable furnace and in a static air atmosphere. The samples were heated at a rate of $120\,°C\,h^{-1}$. Hydrothermally treated membranes were prepared by firing the calcined samples at 600 or 800 °C for 30 h in a 50 mol % steam/air atmosphere at a heating/cooling rate of $100\,°C\,h^{-1}$.

Fig. 1 shows the apparatus used for the hydrothermal treatment of the membranes. The samples were heat treated in a retort (Lindberg) which is a gas-tight steel chamber placed inside a temperature programmable-furnace (Lindberg). Steam was generated by evaporating water in a spherical flask placed in a thermal bath. The temperature of this bath was maintained constant at 87 °C. The steam was mixed with air and the steam/air mixture was introduced into the retort. To prevent condensation of water on the inner walls of the steam delivery line, the temperature of the line was maintained at 120 °C. Circulation of steam inside the retort and above the samples was assisted by vacuum.

### 2.3. Characterization

All unsupported membranes (dried, calcined, hydrothermally treated) were analysed by nitrogen adsorption/desorption at liquid nitrogen temperature (77 K) using an ASAP 2000 Micromeritics instrument. Fast specific surface area measurements were performed with a Gemini 2360 Micromeritics

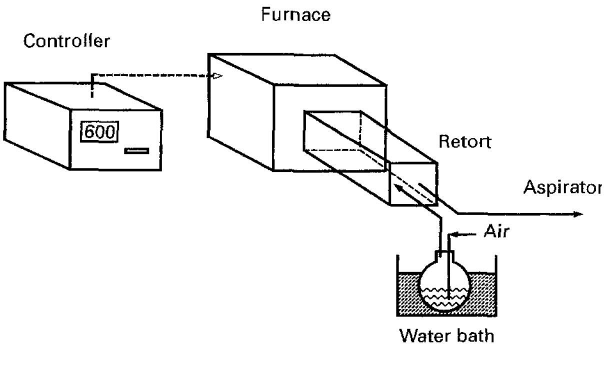

*Figure 1* Experimental apparatus for hydrothermal treatment of pure and doped silica membranes.

instrument using a five-point BET analysis and nitrogen adsorption at 77 K. Micropore analysis was performed in the adsorption porosimeter (ASAP 2000 Micromeritics with micropore capability) using argon adsorption at very low relative pressures ($P/P_0 < 10^{-5}$) and at liquid argon temperature (87 K). The Horvath- Kawazoe model was used to obtain the micropore size distribution of the samples [25]. X-ray diffraction (XRD) analysis of the samples was done in a Philips instrument using Cu$K_\alpha$ radiation. Simultaneous thermogravimetric (TGA) and differential thermal analyses (DTA) were performed with a differential scanning calorimeter (STA 1500H, PL-Thermal Sciences) in flowing nitrogen using a heating rate of 10 °C min$^{-1}$.

## 3. Results and discussion

### 3.1. Pure silica membranes

A typical adsorption/desorption isotherm of the pure silica membranes after drying is shown in Fig. 2. It is type I, characteristic of microporous materials, with no hysteresis between adsorption and desorption [3]. The plateau region corresponds to filling of the micropores with adsorbate molecules. Accurate argon adsorption measurements of these membranes at very low relative pressures resulted in adsorption isotherms like the one shown in Fig. 3. These data were used to calculate the micropore size distribution shown in Fig. 4. The pore-size distribution is quite narrow with a median pore diameter of 0.6 nm. The specific surface area of the dried membrane was 925 m$^2$ g$^{-1}$ and the specific pore volume was 0.46 ml g$^{-1}$. Similar results have been obtained by others [14]. It must be noticed that the BET area is used here only as an approximation of the specific surface area of the samples and for the sake of comparison, because it has no original physical significance in micropore analysis.

The BET surface area and pore volume of the membranes treated under different conditions are shown in Table I. After calcination the specific surface area and the micropore volume of the pure silica membrane reduced by 35% and 75%, respectively. Hydrothermal treatment at 600 °C resulted in an additional 77% surface area reduction and 78% micropore volume loss. When the membrane was hydrothermally treated at 800 °C, complete closure of the micropores and densification of the membrane took place. These results agree with previous studies that showed similar effects of steam and heat on the stability of silica [4, 17, 26, 27]. TGA analysis showed that approximately 17% weight loss occurred up to 100 °C from the removal of physically adsorbed water. Heating up to 900 °C resulted in an additional 5% weight loss which is attributed to the removal of chemically bonded water and organic residuals.

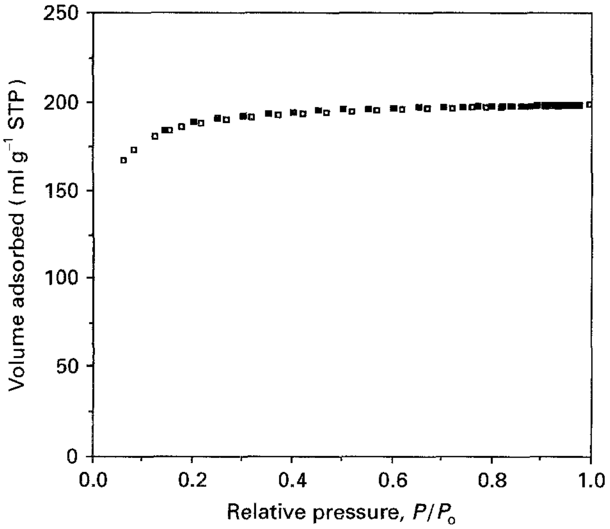

*Figure 2* Nitrogen (□) adsorption/(■) desorption isotherm of dried pure silica membrane.

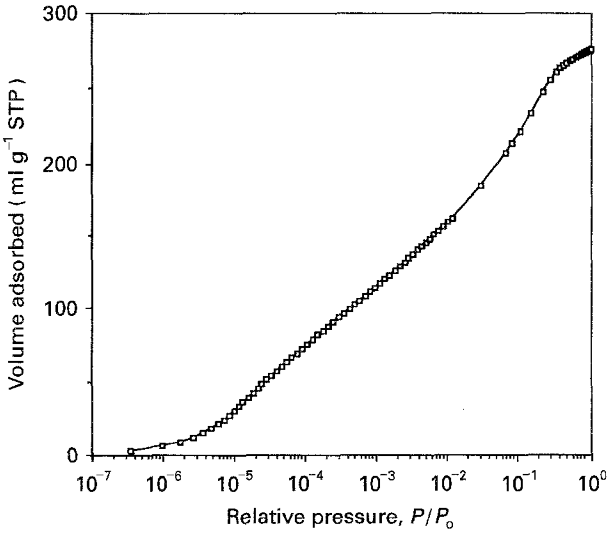

*Figure 3* Argon adsorption isotherm of dried pure silica membrane.

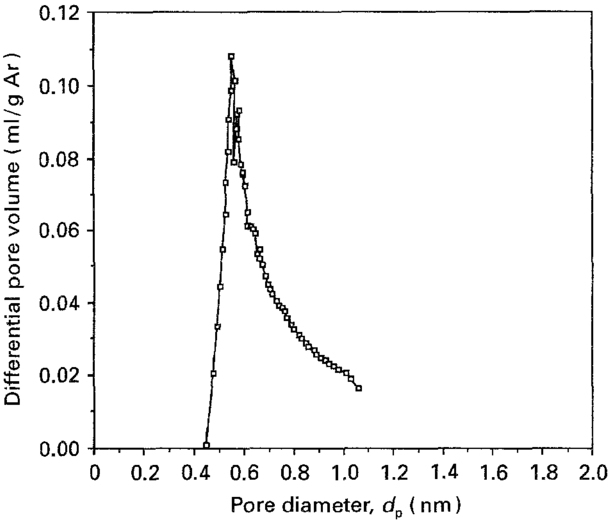

*Figure 4* Micropore size distribution of dried pure silica membrane.

### 3.2. Alumina-doped membranes

Doping with 3% alumina did not change the structural characteristics of the silica membranes which remained microporous after calcination at 400 °C. This can be seen by comparison of the adsorption isotherms of pure and alumina-doped silica membranes as shown in Fig. 5. Both isotherms are

TABLE I Specific surface area and micropore volume changes during heat treatment

| | Pure silica | | Al-doped, 3% | | Al-doped, 6% | Mg-doped, 3% |
|---|---|---|---|---|---|---|
| | $S_{BET}$ $(m^2 g^{-1})$ | $V_p$ $(cm^3 g^{-1})$ | $S_{BET}$ $(m^2 g^{-1})$ | $V_p$ $(cm^3 g^{-1})$ | $S_{BET}$ $(m^2 g^{-1})$ | $S_{BET}$ $(m^2 g^{-1})$ |
| Dried, 40 °C, 48 h | 920 | 0.458 | 962 | 0.481 | 714 | 340 |
| Calcined, 400 °C, 3 h | 604 | 0.114 | 555 | 0.098 | 608 | 252 |
| Hydrothermally treated, 600 °C, 30 h | 142 | 0.025 | 350 | 0.065 | 352 | 50 |
| Hydrothermally treated, 800 °C, 30 h | ~0 | ~0 | 6 | ~0 | ~0 | ~0 |

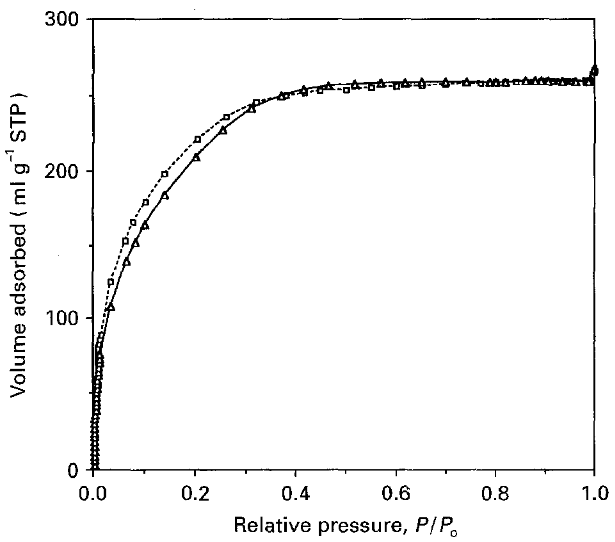

*Figure 5* Argon adsorption isotherms of (□) pure silica and (△) 3% alumina-doped silica membranes calcined at 400 °C for 3 h in static air.

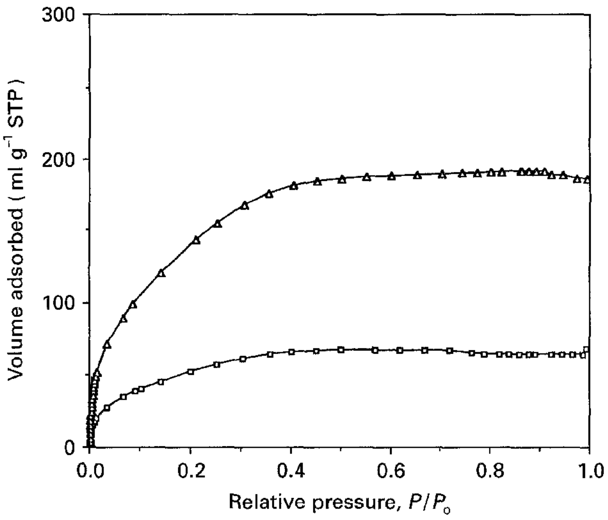

*Figure 6* Argon adsorption isotherms of (□) pure silica and (△) 3% alumina-doped silica membranes, hydrothermally treated at 600 °C for 30 h in 50 mol % steam.

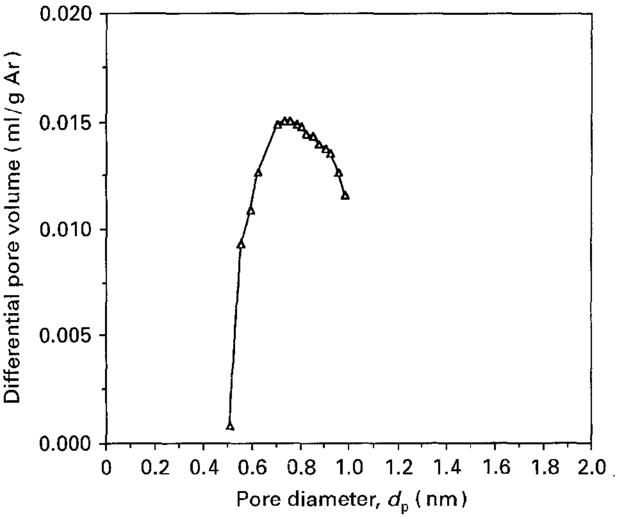

*Figure 7* Micropore size distribution of 3% alumina-doped silica membrane, hydrothermally treated at 600 °C for 30 h in 50 mol % steam.

type I and are very similar to each other. The surface area and pore volume reduction after calcination of the alumina-doped membrane was approximately 42% and 80%, respectively. Upon hydrothermal treatment at 600 °C, the specific surface area of the 3% alumina-doped silica membrane reduced by 37% and the micropore volume reduced by 34% as can be seen from Table I. Comparison of these results with those obtained with pure silica shows that a significant improvement of the hydrothermal stability of the membranes has been achieved under these conditions. This improvement can be more clearly illustrated by comparing the adsorption isotherms of pure and alumina-doped silica membranes hydrothermally treated at 600 °C as shown in Fig. 6. The adsorption isotherm of the pure silica lies below that of the alumina-doped one indicating that the latter retains to a large extent the pore structure intact. The micropore size distribution of this membrane remains narrow with a median pore size of about 0.7 nm as shown in Fig. 7. However, when the alumina-doped membranes were hydrothermally treated at 800 °C, complete pore closure was observed as in the case of pure silica membranes. The improvement of the hydrothermal stability by doping with alumina is therefore limited to a narrow temperature range of 400–800 °C. Increasing the amount of aluminium in the sol from 3% to 6%

was not advantageous, because the obtained improvement in the hydrothermal stability was comparable to that for 3% doping. Independent studies with alumino-silicates showed that high Al/Si atomic ratios can cause changes in the pore structure and the form of the final products [28]. TGA analysis of the 3% alumina-doped membranes gave similar patterns with those of pure silica. Both the calcined and the hydrothermally treated samples were X-ray amorphous, indicating that no crystalline alumina was precipitated under these conditions.

### 3.3. Magnesia-doped membranes

Doping with magnesia was not favourable to the thermal and hydrothermal stability of the membranes. The dried magnesia-doped membranes had specific surface areas that were 50% lower compared to pure silica membranes as shown in Table I. This indicates possible changes in the pore structure caused in the presence of MgO. Because of these changes in the nanostructure of the membranes, doping with magnesia is not an appropriate strategy for improving the hydrothermal stability of the silica membranes. The weight loss pattern of this membrane obtained by TGA analysis was similar to that for pure silica and alumina-doped samples. About 15% weight loss occurred up to 100 °C from the removal of water. Chemically-bonded water and organics were removed in the temperature range 150–600 °C and resulted in an additional 15% weight loss.

### 3.4. Mechanism

Studies concerned with the ageing behaviour and the structural changes of silica–alumina cracking catalysts were carried out in the past [29, 30]. It was found that the influence of heat and steam was the same for both pure silica and silica–alumina gels at the initial stages of ageing but after extensive exposure to steam, silica–alumina catalysts were more stable. To explain these experimental observations, a mechanism was postulated according to which growth of larger gel particles occurred at the expense of smaller ones accompanied by sintering of a large number of primary particles [31]. Furthermore, it was assumed that these two processes proceeded at a larger extent in pure silica and developed stresses in the gel that collapsed its porous structure. Such a mechanism, however, is not applicable to sol–gel derived silica membranes or films prepared through the polymeric (acid-catalysed) route. These gels consist of a polymeric silica network with a low degree of cross-linking [22]. In such systems, the mechanism under which various dopants inhibit or promote densification has to be related to the modification of the silica gel network caused by these dopants.

The silica network consists of tetrahedrally coordinated units and can contain a limited number of octahedral units [32]. Aluminium has an octahedral ionic coordination and under favourable conditions it can substitute some silicon atoms in the silica network. This is supported by electrophoretic mobility measurements which showed that alumino-silicates possess more negatively charged surfaces compared to pure silica, indicating aluminium ion substitution into silicon sites [28]. This is similar to the substitutional defects that aluminium creates when it is used to dope $TiO_2$ promoting the formation of the rutile phase [21]. For this reason, alumina is considered to be a network former. Thus, it inhibits structural changes during thermal and hydrothermal treatment by making the network more rigid.

Magnesia, on the other hand, is known to be a network modifier, because it can break three-dimensional gel networks [32]. In this manner, the silica network becomes weaker and more susceptible to collapse. In addition, magnesia is commonly used as an additive in silica glasses to increase their fluidity and in alumina to promote sintering [32, 33]. Because sintering of amorphous silica proceeds by a viscous flow mechanism, it is possible that magnesia promotes sintering and densification of the membranes by reducing the viscosity of silica. Although the proposed mechanism used to explain the effects of alumina and magnesia on the densification behaviour of silica in the presence of steam are supported by the experimental results presented here, more detailed studies including chemical and surface analysis techniques are required for a more quantitative explanation.

## 4. Conclusion

Unsupported silica membranes were prepared by the sol–gel process. These membranes were microporous with average pore diameter of 0.6 nm. Hydrothermal treatment at 600 °C for 30 h resulted in substantial reduction in the specific surface area accompanied by micropore closure. Complete densification was obtained at 800 °C. The hydrothermal stability of the membranes was improved by doping the starting sol with an aluminum salt. This improvement was obtained for the temperature range 400–800 °C. At 800 °C, and under the same conditions, alumina had no effect on the stability of silica. Alumina did not alter the pore structure of the membranes. Doping with magnesia caused structural changes in the membranes. The effects of alumina and magnesia on the hydrothermal stability of silica membranes were explained in terms of their ability to modify the silica network. In the case of alumina, the network modification is favourable as the latter becomes more rigid and, therefore, more resistant to densification in the presence of steam. In the case of magnesia, however, this modification is detrimental as siloxane bond breakage is likely to take place.

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