

Effects of La_2O_3 addition on the thermal stability of $\gamma\text{-Al}_2\text{O}_3$ gels

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Received 12 February 2003; received in revised form 3 March 2003; accepted 6 April 2003

Abstract

The effects of La_2O_3 additions up to 5 wt.% on the thermal stabilities of sol-gel derived alumina gels were studied. Observations were made on pore size, total pore area, phase changes at various sintering temperatures and times. XRD, Hg-porosimeter, DTA–TG techniques were employed. The addition of La_2O_3 to the sol-gel derived alumina gels raised the $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ transformation temperature to 1200 °C. This significantly improves the thermal stabilities of alumina gels, that are employed in ceramic membranes.

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1. Introduction

Aluminium oxide (Al_2O_3) is known to exist in a number of metastable polymorphs in addition to the thermodynamically stable alpha alumina ($\alpha\text{-Al}_2\text{O}_3$, hexagonal) or corundum [1]. These polymorphs include gamma (γ , cubic spinel), delta (δ , tetragonal), theta (θ , monoclinic). Other types of polymorphs have been also reported [2] such as eta (η , cubic spinel), kappa (κ , orthorhombic), chi (χ , cubic), beta (β , hexagonal).

It has been noted that the starting phase of alumina polymorphs may vary, depending on the processing techniques and conditions, and the phase transformation sequence can take place by various routes. For example, a normally reported transformation route for the sol-gel derived gels is; amorphous $\rightarrow \gamma \rightarrow \theta + \delta \rightarrow \alpha$ in which the transformation products at each stage may be a mixture of several phases [3].

Transformation of metastable alumina phases to $\alpha\text{-Al}_2\text{O}_3$ has been studied by many authors and also the effects of some oxides to these transformations have been reported. As a result it was reported that oxides such as Fe_2O_3 , $\alpha\text{-Al}_2\text{O}_3$, CuO , V_2O_5 [2,4,6] enhanced the phase transformation to $\alpha\text{-Al}_2\text{O}_3$, on the other hand there are reports that some oxides such as SiO_2 , Cr_2O_3

and La_2O_3 [2,3,5,7] inhibited the phase transformation to $\alpha\text{-Al}_2\text{O}_3$.

The polymorphs of alumina (or transition aluminas) are mainly characterized with their high surface areas (especially $\gamma\text{-Al}_2\text{O}_3$). With its very high surface area $\gamma\text{-Al}_2\text{O}_3$ finds applications as micro- and ultra-filtration layers in ceramic membranes and as a catalyst support layer. Ceramic membranes are technically important in separation and filtration as well as in catalytic reactions, because of some unique characteristics in comparison with polymeric membranes, such as chemical stability, long life and good defouling properties.

There were limited reported studies on the thermal stability of $\gamma\text{-Al}_2\text{O}_3$ inorganic membrane top layers. Kaizer and coworkers [8] determined the pore size of top layers of $\gamma\text{-Al}_2\text{O}_3$ membrane for different sintering temperatures. Larbot and coworkers [9] have reported data of pore size vs sintering temperatures (500–1000 °C) for the $\gamma\text{-Al}_2\text{O}_3$ top layers in several publications. However these published papers, have mainly dealt with synthesis of ceramic membranes and their characterization rather than with their thermal stability.

Chen et al. [10] reported that, up to now, there are no reports related to the improvements of the thermal stability of $\gamma\text{-Al}_2\text{O}_3$ catalytic membranes. Unlike the statement of Chen et al. [10], there are reports related to the improvements of the thermal stability of $\gamma\text{-Al}_2\text{O}_3$ with the additions of various oxides to the sol-gel derived alumina gels and top layers. Starting from early

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1990s, alumina based ceramic membranes have been studied extensively by our group and results were published in several publications [5,11–13]. Thermal stability of sol–gel derived alumina gels with and without oxide additives were centre of these studies. Effects of Cr_2O_3 and La_2O_3 additions on the thermal stabilities of alumina gels up to 1100°C were already reported [5].

In the present work, based on our previous results on La_2O_3 additions [5], the amount of additions were kept very narrow such as 1–5 wt.% with 1% increments and also the sintering temperature was raised to 1200°C . The sintering time was also studied as an important parameter on the thermal stability of γ -alumina especially at higher temperatures.

2. Experimental procedures

The preparation of alumina sol and gels, was carried out by using Boehmite (AlOOH) powders (Keith Ceramics Ltd, UK) as a source of Al_2O_3 and La-nitrate [$\text{La}(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$] (Sigma Chemicals, USA), was used as the source of La_2O_3 . Distilled water and HNO_3 were also used in the preparation of alumina gels.

First, Boehmite powders were introduced into hot water (80°C) under stirring, then HNO_3 [mole ratio of $\text{HNO}_3:\text{AlO}(\text{OH}) = 0.07$] was added into the sol for adjusting the pH to 2. La-nitrate [mole ratio of La-nitrate:Boehmite = 0.006 and 0.01] solution was added to the sol. Gelation of the Boehmite sols with and without La-nitrate additions took place in 3 h. These gels were dried at 100°C , for 48 h in an oven. Dried gels were calcined at $700\text{--}1200^\circ\text{C}$ for 1–48 h. Alumina gels were coded as Al-0, Al-1, Al-2, Al-3, Al-4 and Al-5, indicating the wt.% of La_2O_3 in the gels.

Boehmite sols were characterized by measuring the zeta-potential values and particle size distribution of boehmite powders in aqueous suspensions by using Malvern Zeta-sizer 3 equipment.

Characterization of gels were carried out by employing DTA–TG, XRD and Hg-porosimeter techniques for their thermal behaviours, phases, pore sizes, pore size distributions and total pore areas.

3. Results and discussion

In some of the characterization studies such as, DTA–TG, XRD and some Hg-porosimetry, only Al-0, Al-2 and Al-4 gels were studied for comparison instead of all the gels.

3.1. Zeta-potential and particle size measurements

In order to have a stable boehmite suspension (sol), the behaviour of this powder in aqueous solution with

changing pH was measured. The result was shown in Fig. 1. It can be seen clearly that boehmite powders had highest zeta-potential values (typically around 30 mV) at low pH range between 3 and 5. This result indicates that a low pH value is required in order to have a stable boehmite sol in aqueous medium.

By employing the same equipment, particle size distribution of boehmite powders in aqueous sol was measured and the result was shown in Fig. 2. As seen from the figure that particle size of powders were centred around 300 nm. Due to the dispersion problems in the sol, there was a wide particle size distribution in the present boehmite sol. This behaviour can be explained by the agglomeration tendency of very fine ceramic powders due to their high surface energies.

3.2. DTA–TG analysis

DTA–TG curves for the alumina gels containing 0, 2, 4 wt.% La_2O_3 coded as Al-0, Al-2 and Al-4 are depicted in Fig. 3. In the alumina gel sample coded Al-0, there were three clear peaks (two endothermic and one exothermic peaks). The first endothermic peak centered around 125°C and similar in all the gels. This peak corresponds to the removal of water present in the pores. The origin of the second endothermic peak, which was centered around 425°C in all the gels, was

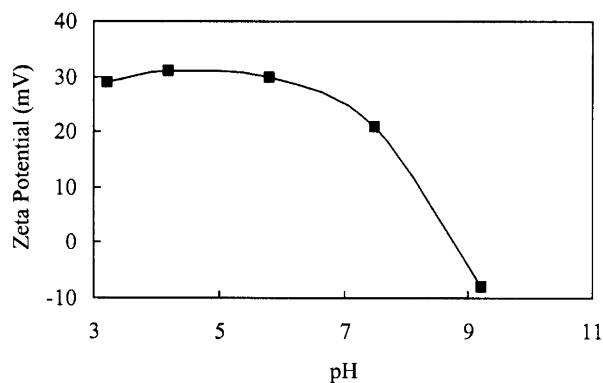


Fig. 1. Zeta potential vs pH behaviour of Boehmite sol.

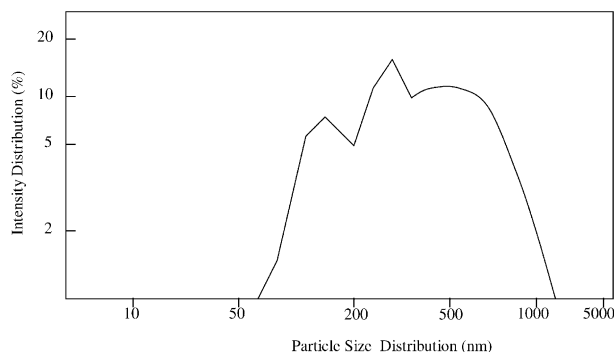


Fig. 2. Particle size distribution of Boehmite sol.

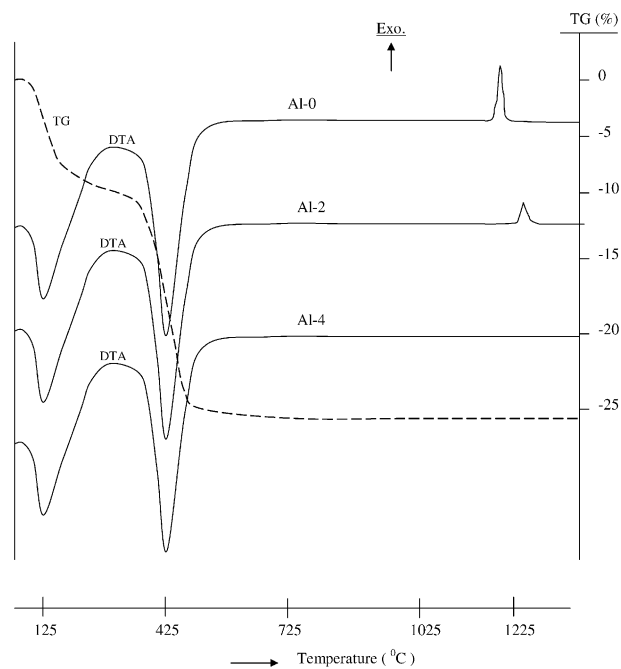


Fig. 3. Thermal behaviours of (DTA–TG diagrams) Al-0, Al-2 and Al-4 gels.

attributed to the removal of hydroxyl groups ($\gamma\text{-AlOOH} \rightarrow \gamma\text{-Al}_2\text{O}_3 + \text{H}_2\text{O}$) and of residual nitrates. The nitrates come from the nitric acid and La-nitrate used as the source of La_2O_3 . There were not any clear endothermic peaks between 600 and 1000 °C in any of the samples as also claimed by Chen et al. [10]. There were some small shifts in the base line but it was very difficult to identify them as endothermic peaks. At temperatures less than 1000 °C, there was no difference in DTA curves of all three gels. Above 1000 °C, there were clear differences in gels and a very clear exothermic peak was observed around 1200 °C in AL-0 gel. This peak corresponds to the formation of $\alpha\text{-Al}_2\text{O}_3$. In contrast, no such exothermic peak is visible in AL-4 gel which contains 4 wt.% La_2O_3 . In AL-2 gel with 2 wt.% La_2O_3 addition, exothermic peak at around 1250 °C, was not sharp and small compared to that of Al-0 gel. These results indicated that, the additions of La_2O_3 to alumina gels affected the transformation of $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$. These findings were supported by the XRD studies. TG results were very similar in all the gel samples and two step weight losses were observed. The first region was up to 250 °C (centered around 125 °C) with a weight loss of ~15%. The second area was up to 600 °C (centered around 425 °C), with a weight loss of further ~10%. The total weight loss was ~25% in all alumina gel samples. Above 600 °C, no further weight losses were observed.

3.3. XRD analysis

Fig. 4a–c show the XRD results of Al-0, Al-2 and Al-4 gels after calcining at various temperatures starting

from 700 to 1200 °C for 1 h soaking time. At 700 and 900 °C, there was not any differences in XRD patterns of all the gels. Crystalline phases were mainly $\gamma\text{-Al}_2\text{O}_3$, with some $\theta\text{-Al}_2\text{O}_3$. It is difficult to distinguish the $\delta\text{-Al}_2\text{O}_3$ phase in the XRD spectra, so $\theta\text{-Al}_2\text{O}_3$ stands for both $\delta\text{-Al}_2\text{O}_3$ and $\theta\text{-Al}_2\text{O}_3$. At 1000 °C, differences start to appear on XRD spectra between the alumina gels with and without La_2O_3 additions. In AL-0 gel there were more $\theta\text{-Al}_2\text{O}_3$ phases compared to the gels with La_2O_3 additions. $\alpha\text{-Al}_2\text{O}_3$ phase started to appear in XRD spectra of Al-0 gel at 1100 °C. There were $\theta\text{-Al}_2\text{O}_3$ peaks as well but the $\gamma\text{-Al}_2\text{O}_3$ peaks were nearly absent. In La_2O_3 added gels, phases were nearly $\gamma\text{-Al}_2\text{O}_3$ and $\theta\text{-Al}_2\text{O}_3$, only there were very small peaks related to $\alpha\text{-Al}_2\text{O}_3$ phase. There were striking differences in three of the gels after calcining at 1200 °C. $\gamma\text{-Al}_2\text{O}_3$ and $\theta\text{-Al}_2\text{O}_3$ transformed to well defined $\alpha\text{-Al}_2\text{O}_3$ with no trace of transition phases in AL-0 gel. In contrast, there is nearly no detectable $\alpha\text{-Al}_2\text{O}_3$ in the XRD spectra of Al-4 gel. In Al-2 gel, there were distinctive $\alpha\text{-Al}_2\text{O}_3$ peaks along with $\theta\text{-Al}_2\text{O}_3$ peaks. These XRD results indicate that the additions of La_2O_3 to the sol-gel derived alumina gels retarded the formation of $\alpha\text{-Al}_2\text{O}_3$ from $\gamma\text{-Al}_2\text{O}_3$ and also the amount of La_2O_3 addition had important effect on the transformation of $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$. It was clearly seen from the XRD results that the thermal stability of $\gamma\text{-Al}_2\text{O}_3$ or the transition aluminas (γ -, δ -, and θ - together) were increased up to 1200 °C, by the addition of 4 wt.% La_2O_3 .

3.4. Surface area and pore characterizations

Surface area, pore size and pore size distribution of alumina gels up to 5% La_2O_3 addition (samples Al-0, Al-1, Al-2, Al-3, Al-4 and Al-5) were measured by Hg-porosimeter. Characterization of the gels were carried out at the sintering temperatures starting from 700 °C to 1200 °C for 1 h. In order to study the effect of sintering time, sintering were applied to all the gels up to 48 h at 1000 °C. Fig. 5 shows the effect of temperature on the surface area (total pore area) of all the alumina gels. As can be seen, there is a gradual decrease in the surface areas of the gels with increasing temperatures. In Al-0 gel, the decrease in surface area was higher compared to the other gels especially after 1000 °C. Until 1000 °C, the decrease was similar in all gels and surface areas were in the range of 104–141 m^2/g and the lowest one was Al-0 gel. After 1000 °C, the decrease was high in Al-0 as the values of surface areas were 54.7 and 9.2 m^2/g , at 1100 and 1200 °C, respectively. On the other hand, the surface areas of the La_2O_3 added gels were in the range of 80–103 m^2/g at 1100 °C, and 24–40 m^2/g at 1200 °C. These results showed that the addition of La_2O_3 to alumina gels was effective on their thermal stabilities at higher temperatures.

In Fig. 6, the effect of temperature on the pore size of alumina gels is shown. As clearly seen from the figure that, up to 1100 °C there were small increases in pore diameter in all the gels. Above 1100 °C, the increase in pore diameter of Al-0 gel, was very sharp compared to the other gels. As an example; the pore diameter of Al-0 gel at 1100 °C was 13.2 nm compared to 12.1 nm of Al-0 gel. The pore diameters were 58.7 and 12.9 nm for Al-0 and Al-2 at 1200 °C, respectively. With the given temperature and time, the thermal stability of alumina gel

without La₂O₃ addition was stable up to 1100 °C. But, it is also known that the time of sintering has important effect on the thermal stability. For this reason, sintering time was changed from 1 h up to 48 h, at 1000 °C in order to see how the gels behaved at longer times. Fig. 7 shows the changes in total pore area of all the gels with increasing sintering times. As seen from the figure that there is a gradual decrease on surface area of all the gels. But, this decrease was higher in Al-0 gel for all sintering times. In La₂O₃ added gels (Al-1–Al-5), the decrease in

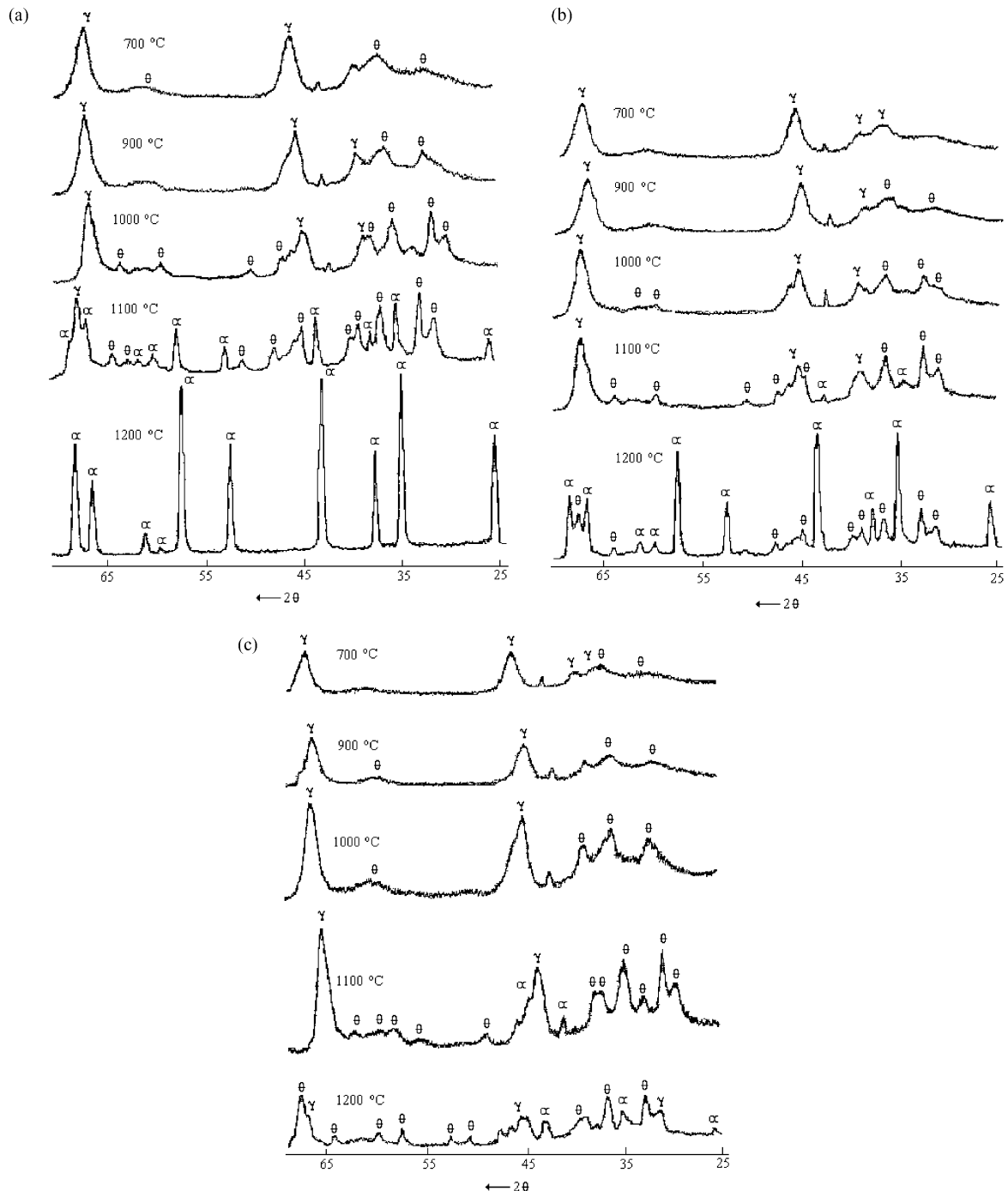


Fig. 4. XRD results of alumina gels at various sintering temperatures for 1 h, (a) Al-0 gel, (b) Al-2 gel and (c) Al-4 gel.

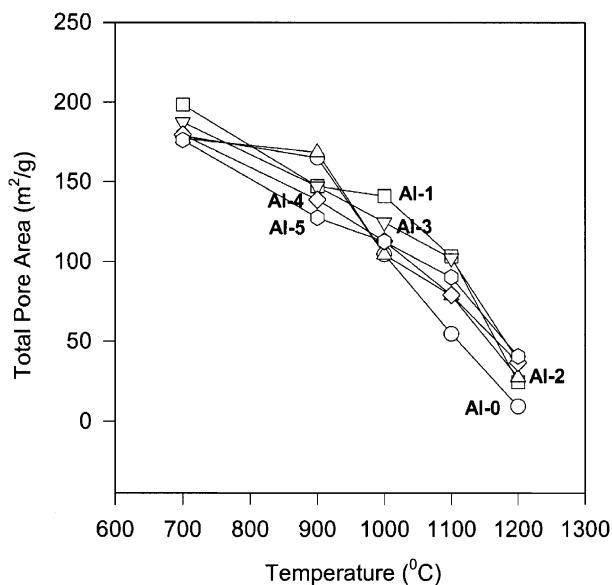


Fig. 5. Total pore area vs sintering temperatures of alumina gels.

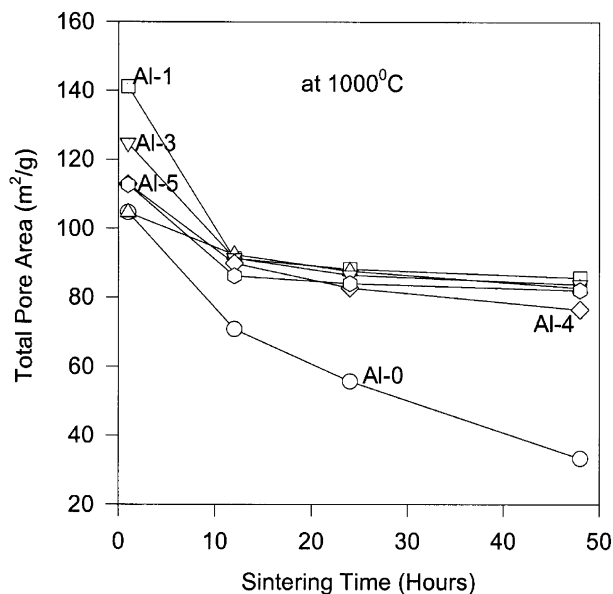


Fig. 7. Changes in total pore area of alumina gels with increasing sintering times at 1000 °C.

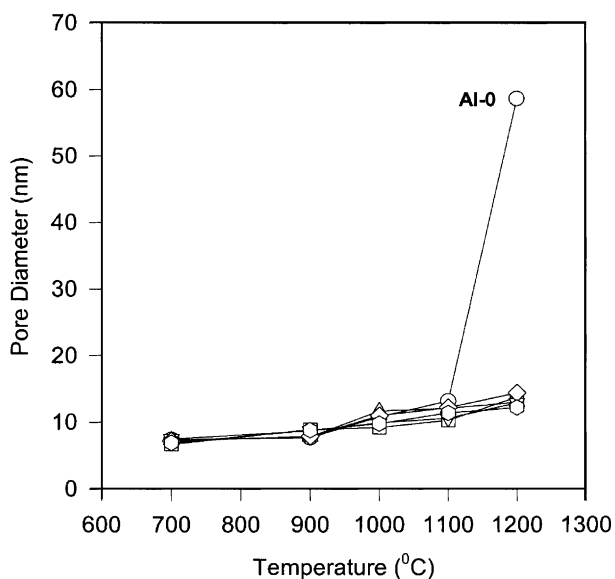


Fig. 6. Changes in pore diameter of alumina gels with increasing sintering temperatures.

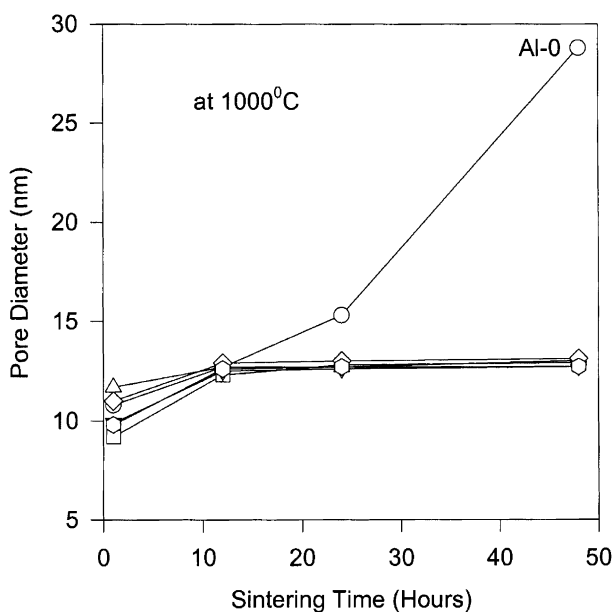


Fig. 8. Changes in pore diameter of alumina gels with increasing sintering times at 1000 °C.

surface area was nearly the same for all sintering times. After 48 h sintering at 1000 °C, the surface areas were 33.3 and 85.6 m²/g for Al-0 and Al-1 gels respectively. The surface areas of all the La₂O₃ added gels were in the range of 76–86 m²/g, after sintering at 1000 °C for 48 h.

The changes in pore diameter of all the gels with increasing sintering time at 1000 °C, were shown in Fig. 8. There were small increases in pore diameters up to 12 h and these were similar in all gels. After 12 h the increase in pore diameter of the Al-0 gel was higher and above 24 h, the pore diameter of Al-0 gel showed very sharp

increase compared to La₂O₃ added gels. The changes in pore diameter of all La₂O₃ added gels were very small and gradual. Even after 48 h, the pore diameters of these gels were in the range of 12.7–13 nm. This value was 28.8 nm in Al-0 gel.

Pore diameter measurements only give the mean values of the pore diameter. Pore size distribution gives more information on pore growth with increasing time and temperatures. In order to study the pore size distributions, Al-0, Al-2 and Al-4 gels were chosen. The changes in pore size distribution against sintering temperatures and also sintering times were examined.

Fig. 9a–c show the pore size distribution of Al-0, Al-2 and Al-4 gels against sintering temperatures (from 700 to 1200 °C for 1 h), respectively.

In Fig. 9a, pore size distribution of Al-0 was similar at 700 and 1000 °C. In another word, the pore size distribution was similar up to 1000 °C. Above 1000 °C, the fact that the peaks were broadened and moved towards left in the figure, can be interpreted as increasing pore diameter. Also the pore size distribution became wider. At 1200 °C, the double peak dispersion was obvious compared to single peaks at lower temperatures. In Al-0 gel, the larger and sharper peak moved to the left to

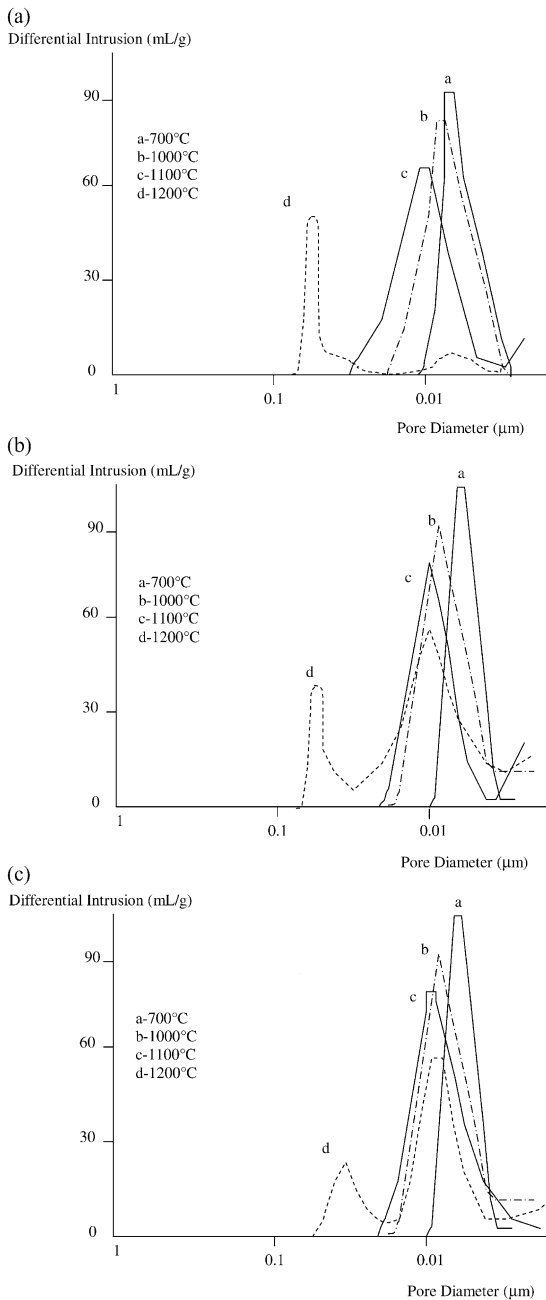


Fig. 9. Pore size distributions of alumina gels with increasing sintering temperatures: (a) Al-0 gel, (b) Al-2 gel and (c) Al-4 gel.

larger pore diameter side and the peak in small diameter area was very small. This means that most of the pores were concentrated in large pore diameter area. These results were consistent with pore diameter results, where the mean pore diameter of Al-0 was around 58 nm. Pore size distribution of Al-2 and Al-4 gels showed similar

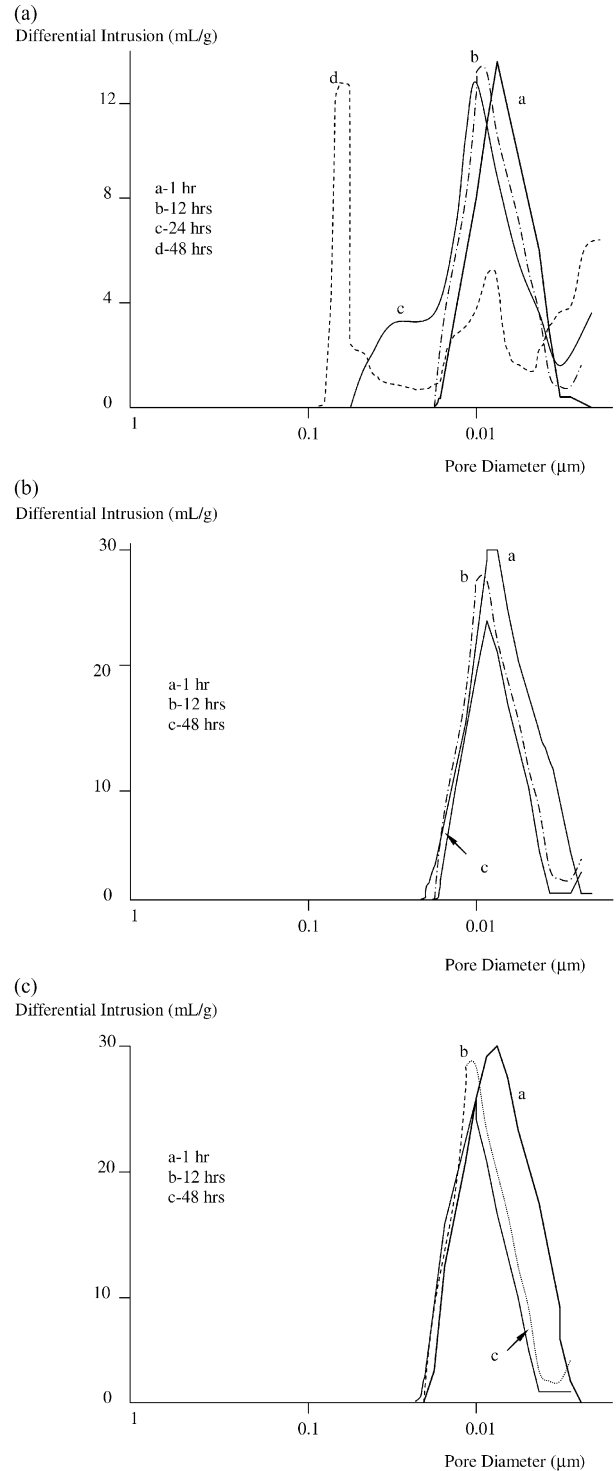


Fig. 10. Pore size distributions of alumina gels with increasing sintering times at 1000 °C: (a) Al-0 gel, (b) Al-2 gel and (c) Al-4 gel.

behaviour with increasing temperatures and at 1200 °C. They also showed double peak dispersions but these double peaks were different from each other and also different than that of Al-0. In Al-2 gel. The second peak in larger pore size area was higher and larger than that of Al-4 gel. In contrast, the peak in small pore size area was broader in Al-4 gel compared to Al-2 gel. Compared to each other, it was easily seen that, all gels showed double peak dispersion at 1200 °C. But, the size and the places of these peaks were different from gel to gel. In conclusion, with increasing temperature, the pore size distribution in Al-0 gel was broader than those of La₂O₃ added gels. Also, the peak in large pore areas was higher and larger in Al-0 gel. These results were consistent with the pore size results.

Fig. 10a–c, show the effect of sintering time on pore size distribution in Al-0, Al-2 and Al-4 gels at 1000 °C, respectively. It can be seen clearly that sintering time was very effective in Al-0 gel. Pore size distribution peaks after 1 and 12 h were similar except that in 12 h the peak moved to the left (pore diameter increased). Pore size distribution peak in 24 h (peak c) started to show a second peak and characterized as double peak dispersion. The width of peak increased with sintering time. After 48 h sintering at 1000 °C, double peak dispersion was obvious and the higher peak was in the left which meant the pore diameter was large. In contrast, there was no double peak dispersion behaviour of pore size distribution in Al-2 and Al-4 gels. These results also showed that the thermal stabilities of alumina gels were increased with the additions of La₂O₃. In order to see the difference more accurately, pore size distribution peaks of Al-0, Al-2 and Al-4 gels at 1000 °C for 48 h were put in the same figure (Fig. 11). It was clear that, Al-2 and Al-4 gels showed very narrow and single peak dispersion of pore size distribution. On the other hand, in Al-0 gel there was very clear double peak dispersion

and the larger portion of the pores were in large pore size area.

All the pore size distribution peaks showed that La₂O₃ addition kept the pore size smaller and also very narrowly distributed at higher temperatures and at longer sintering times.

4. Conclusions

γ -Al₂O₃ (Al-0) and La₂O₃ added (up to 5 wt.%) γ -Al₂O₃ gels were prepared by using Boehmite powders and sol-gel process. La₂O₃ addition at any level improved the thermal stabilities of alumina gels compared to undoped γ -Al₂O₃ gels. Pore characteristics including average pore diameter, pore size distribution and pore surface areas were improved. La₂O₃ addition kept the pore size small and the pore size distribution very narrow even at very high sintering temperatures such as 1200 °C. After sintering at 1200 °C for 1 h, the average pore diameter and total pore area of γ -Al₂O₃ (Al-0) gel were 58.7 nm and 9.2 m²/g respectively, and as a comparison, for the La₂O₃ doped γ -Al₂O₃ gel such as Al-4, these results were 14.4 nm and 36.6 m²/g, respectively. According to the results of the present work, the addition of La₂O₃ on the thermal stability of γ -Al₂O₃ gels is crucial. Even at 1 wt.% La₂O₃ addition level it was very effective in improving the thermal stability of gel-derived γ -alumina gels or membrane layers.

The higher thermal stability of La₂O₃-added gels is related to the retarded phase transformation from γ -Al₂O₃ to α -Al₂O₃. The effect of La₂O₃ on this phase transformation could be explained that the presence of the lanthanum oxide on the γ -Al₂O₃ surface may reduce the possibility of the nucleation of α -Al₂O₃, thus raising the phase transformation temperature.

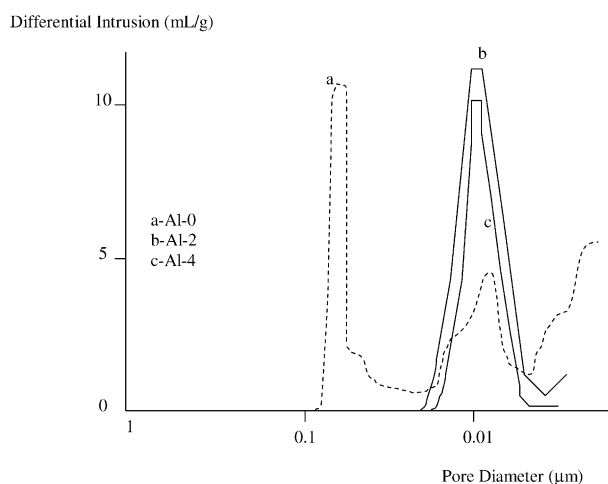


Fig. 11. Pore size distributions of Al-0, Al-2 and Al-4 gels, after sintering at 1000 °C for 48 h.

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