Chapter 2: Mesoporous Silica-Alumina Aerogels Through Hybrid Sol-Gel Route Followed by Non-Supercritical Drying

2.1 Synthesis and Characterisation of non-supercritically dried Silica-Alumina aerogels

2.1.1 Abstract

Silica-alumina mixed oxide aerogels have been synthesised by non-supercritical method, having compositions of 5, 10, 15, 20 and 25 wt% of alumina in silica through a hybrid sol-gel technique. Boehmite was used as the precursor for alumina and TEOS for silica. Subcritical drying method involving repeated solvent exchange and gel wall strengthening is followed in place of supercritical method. The aerogels are calcined at 500, 700, 900 and 1200 °C. Nitrogen sorption studies indicate that the mixed oxide aerogels are mesoporous in nature with high surface areas comparable to supercritically dried aerogels and also possess excellent thermal pore stability. Fourier Transmission Infrared (FT-IR) spectroscopy has been used to study the effect of alumina addition to silica. The linear shrinkage of aerogels upon heat treatment is also reported. The acid strength distribution was measured by temperature programmed desorption of ammonia (TPD). The present method involving hybrid sol-gel route followed by subcritical drying could be further developed for synthesis of many mixed oxide mesoporous hybrids for catalyst and gas adsorption applications.

2.1.2 Introduction

Aluminosilicate aerogels with porous structures reveal very interesting physical properties and have many practical and potential industrial applications, including their
use as acid catalysts due to their good chemical resistance [1-6] as membranes for the separation of gas phases [7] purification of water and reactors [8] as adsorbents [9] as humidity control materials [10] and as starting materials for the synthesis of mullite ceramics [11, 12]. The sol-gel process is an attractive method to synthesise metal catalysts and mixed metal oxide catalysts [5]. The most important step for obtaining a porous ceramic from the precursor gel in a sol-gel process is the removal of solvent and volatiles. Usual drying methods lead to considerable shrinkage of the gel and this introduces stresses which result in the collapse of the gel. Supercritical conditions or critical point drying (CPD) result in aerogels which are characterized by low densities and extremely high porosity [13, 14]. Non-supercritical methods are investigated as an alternative to supercritical route which is generally known to be energy intensive, hazardous and expensive [15, 16]. But it is highly restricted by the large drying stresses developed during drying and the large shrinkages associated with it. The drying stress developed due to the capillary forces and the subsequent shrinkage can be minimized by reducing the capillary force [17-19]. Shrinkage during ambient pressure drying can also be minimized by increasing the stiffness of the gel network. This is achieved by reinforcing the gel network by infiltrating sodium silicate or Tetraethoxy silane (TEOS) prior to drying [20-26]. Deshpande, Smith and Brinker eliminated shrinkage during ambient pressure drying by surface modifying the silica gel by Trimethyl chloro silane (TMCS) prior to drying [27]. The reduction in shrinkage, attributed to ‘spring back effect’ of the gel structure due to repulsion between the hydrophobic caps of surface silanol groups has been used by many researchers [16, 19, 28-31].
During the preparation of mixed oxide aerogels involving silica, if the hydrolysis of the metal alkoxide is faster than that of silicon alkoxide, a non uniform sol results because sedimentation and associated separation take place before gelation. Tamon et al. prepared aerogels by hydrolysing TMOS first, ensuring that no water remains after hydrolysis [3]. Then the aluminium alkoxide was added to obtain uniform Si-O-Al linkages and finally hydrolysed the alkoxide again. Heinrich et al. used chelated aluminium alkoxides in order to reduce reaction rates of [Al (OBu)₃] in comparison with TEOS [32-34]. A double alkoxide was used by Pouxviel [35, 36]. We have used boehmite sol as one of the precursors for the preparation of silica alumina aerogels and hybrid sol-gel route ensures nano-metric scale mixing in heterogeneous systems [31-39].

Pure silica aerogels have limited thermal pore stability since they sinter at temperatures above 600 °C [46-48] and this is detrimental for its use as high temperature insulation materials. Saliger et al. added aluminium oxide and aluminium hydroxide powders to silica and studied the sintering process using dilatometry, viscosity and nitrogen sorption studies [49].

In this chapter the synthesis of silica-alumina aerogels by a hybrid sol-gel route followed by subcritical drying is presented. The aerogels were then calcined at 500, 700, 900 and 1200 °C and were characterized by BET, FT-IR, XRD, & TPD measurements. The bulk density of the as prepared aerogels is also presented. The linear shrinkage of the silica aerogels and the mixed oxide aerogels upon heat treatment were also studied.
2.1.3 Experimental

2.1.3.1 Materials & preparation procedure

Non-supercritical drying method has evolved as a simple method over supercritical drying method for the synthesis of aerogels [16-31]. This involves aging, solvent exchange and drying under controlled conditions. Previous experiments revealed that the mixed oxide gels prepared under high water/alkoxide ratio result in porous gels having high surface area [18]. The gels were immersed in water for 24 hours so as to hydrolyse any unreacted TEOS. Solvent exchange was done with isopropanol to remove water from the pores and was aged in 80% silane solution. The aging process provides strength to the gel network, since dissolution and reprecipitation of silica particles to the gel network takes place [22]. The aging process in 80% silane solution for 48 hours gave the highest surface area [50]. These gels were then solvent exchanged with isopropanol, since solvent exchange reduces capillary stresses [17], and further, liquids of low surface tension and high molecular volume favour the production of gels having high surface area [18].

Boehmite, (AlOOH) (99% purity, alumina content 70%, Condea Chemie, Germany) having BET surface area of 230 m$^2$/g and crystalline size 48-60 Å was used as the precursor for alumina and Tetraethoxy silane (Fluka, Switzerland) for silica. The concentration of alumina in the stock boehmite sol was 0.0107 g/ml. TEOS was mixed with isopropanol (S.D. Fine Chemicals, India) and HCl (pH=1.54) in a molar ratio of 1:4:16 [18]. In a typical experiment for preparing 25 wt% alumina in silica, 3.884g of TEOS in 4.475g isopropanol was hydrolysed using 5.45g of H$^+$ (HCl, pH=1.54). The clear sol was stirred for 30 min, 35 ml boehmite sol was added and the sol was again
stirred for 30 min. Subsequently, the pH was adjusted to 5 using 5% ammonia solution. The visually homogeneous sol was then transferred to vials and kept at 50 °C for gelation.

**Fig. 2.1.1.** Flowchart for the preparation of Silica-Alumina mixed oxide aerogels
The gelation time was noted. The gels were aged for 5 to 6 hours and transferred to water and was kept for 24 hours at 50 °C. It was then washed with isopropanol five times within 24 hours so as to remove water from pores. During the washing process the gels were kept at 50 °C. This was followed by aging the gels in 80% TEOS for 48 hours at 50 °C and the final solvent exchange with isopropanol maintaining the gels at 50 °C. The gels were then dried in tightly closed containers at 70 °C so that the porous structure is retained in the gels by the slow removal of solvent from the pore network. The aerogels obtained after drying at 70 °C were calcined for 3 hours at 500, 900, 700 and 1200 °C. The alumina content was varied from 5 to 25 wt%. The detailed flowchart for the preparation of Silica-Alumina aerogels is presented in Fig.2.1.1.

2.1.3.2 Characterisation of the aerogels

Bulk density of the dried gels was calculated by measuring their mass and volume.

\[
\text{Volume, } V = \frac{\pi d^2 l}{4}
\]

Where \(d\) is the diameter and \(l\) length of the gel.

\[
\text{Bulk Density} = \frac{\text{Mass}}{\text{Volume}}
\]

The Fourier Transform Infrared Spectroscopy of gels and calcined samples was recorded in Nicolet Magna-560-FT-IR Spectrometer (USA) using pellets made out of KBr and dispersed gel powder. The BET surface areas of calcined aerogels were determined by \(N_2\) adsorption at 77K (Micromeritics, Gemini Model 2360, USA). The calcined samples were preheated in a flow of nitrogen for 3 hours at 200 °C to remove all the volatiles and chemically adsorbed water from the surface. Adsorption studies were carried out at liquid nitrogen temperature. The temperature-programmed desorption (TPD) was carried out by keeping 0.5 g of the aerogel sample in a microreactor followed
by degassing at 300 °C for half an hour. The reactor was then cooled to room temperature
and 20 ml ammonia gas was injected through the sample. The gas emerging from the
reactor outlet was scrubbed into known volume of standard sulphuric acid for 15 minutes.
The eluted ammonia was estimated volumetrically using the equation,

\[
\text{Amount of ammonia adsorbed} = (N_{NaOH} \times \Delta V) \times \frac{17}{W} \times 1000 \text{ mmol/g.}
\]

The experiment was repeated at temperatures from 100 to 800 °C. Thermo
tical analysis (TMA) of the aerogels was performed by heating the aerogel pellets
at the rate of 10 °C/ min. under Nitrogen atmosphere using Shimadzu 60 H Thermo
Mechanical Analyser. The X-ray powder diffraction patterns of the calcined samples
were recorded in Philips Diffractometer (PW 1710), Netherlands, using Ni filtered CuKα
radiation. The samples were scanned from 0 to 60° (2θ values) with a step speed of 2.4°/min.

2.1.4 Results and Discussion

The gelation time for silica as well as those containing various alumina
compositions is provided in Table 2.1.1. As the alumina content is increased in silica the
gelation time is prolonged. Huang et al. studied the variation in gel time of silica sol as a
function of either H₂O/TEOS molar ratio or amount of base catalyst added [51]. They
found that increase of water content (as a reactant) would increase the gel time. Here the
TEOS: isopropanol: water was kept constant at 1:4:16, but to obtain higher loadings of
alumina, a larger volume of boehmite sol was required compared with lower alumina
compositions. A composition greater than 25% was difficult to obtain since the alcogel
became very fragile. The bulk density of aerogels ranges from of 0.003 to 0.8 g/cm³ with
high surface area extending up to about 1500 m²/g [52]. The density measurements of the
silica-alumina aerogels and pure silica aerogel prepared are provided in Table 2.1.2. The silica aerogel has a density of 0.401 g/cm³, and the 5, 10 and 15 wt% alumina aerogels possess densities of 0.40, 0.54 and 0.63 g/cm³ respectively. The 20 wt% and 25 wt% alumina aerogels cracked during drying.

Table 2.1.1. Gelation time for mixed oxide gels

<table>
<thead>
<tr>
<th>Alumina content in mixed oxide Sol (wt %)</th>
<th>Gelation time (min)</th>
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<tbody>
<tr>
<td>0</td>
<td>14</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
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<td>10</td>
<td>70</td>
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<td>15</td>
<td>110</td>
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<td>20</td>
<td>150</td>
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<td>220</td>
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Table 2.1.2 Density measurements of silica-alumina aerogels

<table>
<thead>
<tr>
<th>Alumina content in mixed oxide Sol (Wt %)</th>
<th>Density (g/cm³)</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>0.401</td>
</tr>
<tr>
<td>5</td>
<td>0.400</td>
</tr>
<tr>
<td>10</td>
<td>0.54</td>
</tr>
<tr>
<td>15</td>
<td>0.63</td>
</tr>
<tr>
<td>20</td>
<td>Cracked gel</td>
</tr>
<tr>
<td>25</td>
<td>Cracked gel</td>
</tr>
</tbody>
</table>
For the preparation of silica-alumina mixed oxide aerogels the essential prerequisite for ensuring homogeneity is the decomposition of alkoxy and other anionic residues followed by cross-condensation between aluminium and silicon moieties [53]. The cross condensation is initiated around 400 °C [53] and the gels are calcined from 500 °C upwards.

**Fig. 2.1.2.** FTIR spectra of (A) Silica aerogel calcined at 500 °C (B) 25 wt% alumina gel calcined at 500 °C (C) as prepared 25 wt% alumina gel

The FTIR spectra of the as prepared 25 wt% alumina gel and that calcined at 500 °C are provided in Fig. 2.1.2. The FTIR spectrum of 500 °C calcined silica aerogel is also provided. Boehmite is composed of AlO$_6$ octahedra and silica is composed of SiO$_4$ tetrahedra. All Al-O and Si-O related vibrations are known to appear only in the 1200-400 cm$^{-1}$ region [47]. The peak at 3300 cm$^{-1}$ indicates OH vibrations. The peak at 1069 cm$^{-1}$ is characteristic of Si-O-Si vibration while the shoulders appearing at high and lower side of this absorption band indicate the presence of Si-O-Al bonds through cross...
condensation of boehmite and silica [54]. When alumina is added to silica, the silica forces \( \text{AlO}_6 \) in boehmite to \( \text{AlO}_4 \) polyhedron [53]. The bands at 620 cm\(^{-1}\) and 731 cm\(^{-1}\) in the as prepared gels of 25 wt% alumina in silica are characteristic of octahedra Al and tetrahedral Al respectively [53]. This infers that the silica is forcing the \( \text{AlO}_6 \) polyhedra in boehmite to \( \text{AlO}_4 \) tetrahedra. The same aerogel sample calcined at 500 °C shows shoulder peaks appearing at high and lower side of the absorption peak at 1069 cm\(^{-1}\) indicating the presence of Si-O-Al bonds.

![Fig. 2.1.3. Adsorption isotherms of (A) silica (B) 5 wt% (C) 10 wt % (D) 15 wt % (E) 20 wt % and (F) 25 wt % alumina calcined at 500 °C.](image)

The isotherms of silica and mixed-oxide aerogels calcined at 500 °C are provided in Fig. 2.1.3. The isotherm is Type IV which is characteristic of mesoporous materials. The surface area and total pore volume of 500 °C calcined aerogels are provided in Fig.
2.1.4. The figure indicates clearly that as the percentage of alumina increases above 5 wt%, the surface area decreases.

D.R. Dunphy et al. prepared surfactant templated silica-alumina thin films by doping alumina into the pore walls during material synthesis or grafting on to the pore surface of preformed mesophases [55]. There was a decrease in total porosity and surface area with Al doping. On the basis of refractive index data, this decrease was attributed to reduction in pore accessibility and not pore collapse. Similar decrease in surface area was also reported by Hernandez et al. [56]. The authors studied the relationship between the porous texture, the co-ordination number of Al atoms, the type of surface acidity and the sol-gel acidic synthesis conditions at two pH values (pH ≈ 2 and pH ≈ 0) in silica-alumina aerogels made with molar Si to Al ratio \( r_{Si/Al} = 100 \). K. Sinko et al. prepared alumino-silicate aerogels under various conditions and compared with respect to their nanostructures and porosity [57]. The authors found that the Al incorporation into the silicate network did not decrease the porosity in these series. The highly bonded Al content, the loose fractal structure and the very small elementary units derived from gelation of aluminium nitrate or isopropoxide and TEOS guarantee good porosity property hence a high surface area.

The decrease in surface area beyond 5 wt% alumina addition may be attributed to the crystallization of Al in the pores of the aerogel. B. Ameen et al. [58] prepared silver nanoparticles in silica aerogel matrix by subcritical drying. On increasing the silver concentration, the specific surface area decreased from 845 m\(^2\)/g to 307 m\(^2\)/g. The concomitant decrease in surface area with increase in silver concentration showed that fine silver particles crystallise within the pores of the aerogel matrix. Moreover the
largest pore volume was obtained for 1% Ag and it subsequently decreased as percentage of silver is increased. This characteristic was attributed to the partial replacement of silicon by silver atom in the silica framework and the associated vacancy created for the charge compensation. With increasing silver concentration, the silver atoms get crystallised in the pores of the aerogel matrix, reducing the total pore volume.

![Graph showing surface area and total pore volume](image)

**Fig. 2.1.4.** Surface area and pore volume of silica and silica-alumina aerogels calcined at 500 °C.

For silica, a surface area of 736 m²/g and a pore volume of 1.227 cm³/g after calcining at 500 °C was obtained. The surface area of 25 wt% alumina was found to be 266 m²/g, the pore volume was 0.329 cm³/g. The surface area of 5 wt% alumina is higher than that of pure silica calcined at 500 °C. By the addition of 5 wt% alumina to silica, the aerogel network is strengthened and the shrinkage is therefore less when compared to silica aerogel.
Fig. 2.1.5. Adsorption isotherms of (A) silica (B) 5 wt% (C) 10 wt% (D) 15 wt% (E) 20 wt% and (F) 25 wt% alumina calcined at 700 °C.

Fig. 2.1.6. Surface area and pore volume of silica and silica-alumina aerogels calcined at 700 °C.
This is confirmed by the fact that 5 wt\% alumina possesses a total pore volume of 1.3 cm$^3$/g compared to a pore volume of 1.22 cm$^3$/g in the case of pure silica.

The isotherms of silica and mixed oxide aerogels calcined at 700 °C are provided in Fig. 2.1.5. The isotherm is Type IV which is characteristic of mesoporous materials. The surface area and total pore volume for the 700 °C calcined aerogels are provided in Fig. 2.1.6. The figure indicates clearly that as the percentage of alumina increases the surface area and total pore volume decreases. The surface area of 5 wt\% alumina-silica is higher than that of pure silica calcined at 700 °C. By the incorporation of 5\% alumina to silica, the aerogel network is strengthened and as we increase the calcination temperature the alumina sites shield adjacent Si-OH….Si-OH groups preventing the silanol condensation. The same phenomenon is also seen in the case of 10 wt\% alumina aerogel. The surface area of 10 wt\% alumina aerogel is almost same as that of silica. Silica aerogels calcined at 700 °C have a surface area of 583 m$^2$/g with a total pore volume of 0.92 cm$^3$/g. The 10\% alumina-silica aerogel calcined at 700 °C has a surface area of 582 m$^2$/g and a total pore volume of 1.04 cm$^3$/g. The surface area of 5 wt\% alumina calcined at 700°C was found to be 662 m$^2$/g with a total pore volume of 0.99 cm$^3$/g and that of 25 wt\% alumina calcined at 700 °C was found to be 246 m$^2$/g with a pore volume of 0.31 cm$^3$/g.

The isotherms of silica and mixed-oxide aerogels calcined at 900 °C are provided in Fig. 2.1.7. The surface area and total pore volume of silica and silica-alumina aerogels calcined at 900 °C are provided in Fig. 2.1.8. As in the case of 500 °C aerogel sample the surface area decreases as the percentage of alumina in silica increases from 5 wt\% to 25 wt\%. For pure silica aerogel, the surface area was found to be 415 m$^2$/g with a pore
Fig. 2.1.7. Adsorption isotherms of (A) Silica (B) 5 wt% (C) 10 wt% (D) 15 wt% (E) 20 wt% and (F) 25 wt% alumina calcined at 900 °C.

Fig. 2.1.8. Surface area and pore volume of silica and silica-alumina aerogels calcined at 900 °C.
volume of 0.73 cm$^3$/g and for 25 wt% alumina the surface area was 156 m$^2$/g with a pore volume of 0.24 cm$^3$/g. The isotherms of mixed-oxide aerogels calcined at 1200 °C are provided in Fig. 2.1.9. The surface area and total pore volume of silica and silica-alumina aerogels calcined at 1200 °C are provided in Table 2.1.3. The silica and 5 wt% alumina-silica aerogel loses its surface area when calcined at 1200 °C and for 15 and 25 wt% alumina aerogels the surface areas are 88 and 70 m$^2$/g respectively. The pore volumes for 15 and 25 wt% alumina are 0.15 cm$^3$/g and 0.11 cm$^3$/g respectively. Surface area and Pore volume of silica and silica-alumina aerogels calcined at 500, 900 and 1200°C are provided in Table 2.1.3. The specific surface area and pore volume for the gels decrease with increase in calcination temperatures. The most obvious physical change that occurs when an amorphous gel is heated above room temperature is shrinkage. The physical and chemical changes that occur during the heat treatment of the aerogels are studied in detail [59]. Above 600 °C viscous sintering starts in the silica gel network [46-48] and this will cause a further decrease in surface area at a temperature of 1000 °C. The silica and 5 wt% alumina aerogel completely lose surface area after calcining at 1200 °C. The reduction in surface area is due to the densification of secondary particles leading to pore collapse. The pore radius increases as the calcination temperature increases for silica and mixed oxide aerogels. The slight increase in pore size for aerogels as we increase the calcination temperature may be due to the fact that the primary particles collapse to form larger pores. The incorporation of aluminium atoms into the silica network has a significant influence on the macroscopic properties of the aerogels [60]. Pure silica aerogels calcined at 1200 °C has a surface area much below the value one, (nearly no adsorption).
By the incorporation of 15 wt% and 25 wt% of alumina, the surface area was increased from zero to 88 m$^2$/g and 70 m$^2$/g, respectively. The thermal pore stability of silica is increased by the addition of alumina. The aluminium sites shield adjacent Si-OH...OH-Si groups thus preventing the dehydroxylation and silanol condensation and also reduce the number of hydrogen bonds. The densification of secondary particles leading to pore collapse is prevented by the presence of alumina. Himmel et al. [60] investigated the linear shrinkage of subcritically dried 70% SiO$_2$-30% Al$_2$O$_3$ aerogel and found that the linear shrinkage was only 25% when compared with silica aerogel which showed a linear shrinkage of 48%. Saliger et al. gave a description of the shrinkage associated with supercritically dried silica aerogel into which dried aluminium oxide and aluminium hydroxide powders were integrated during sol-gel process [49].
Table 2.1.3. Surface area and pore volume of silica and silica-alumina aerogels calcined at 500, 700, 900 and 1200 °C.

<table>
<thead>
<tr>
<th>Alumina content in mixed oxide Sol (wt %)</th>
<th>Calcination temp. (°C)</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>500</td>
<td>736</td>
<td>1.23</td>
<td>66</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>583</td>
<td>0.91</td>
<td>62</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>415</td>
<td>0.73</td>
<td>70</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>5</td>
<td>500</td>
<td>796</td>
<td>1.3</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>662</td>
<td>0.99</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>398</td>
<td>0.79</td>
<td>80</td>
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<tr>
<td></td>
<td>1200</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<tr>
<td>15</td>
<td>500</td>
<td>420</td>
<td>0.57</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>700</td>
<td>359</td>
<td>0.48</td>
<td>53</td>
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<td></td>
<td>900</td>
<td>232</td>
<td>0.41</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>1200</td>
<td>88</td>
<td>0.15</td>
<td>72</td>
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<tr>
<td>25</td>
<td>500</td>
<td>266</td>
<td>0.33</td>
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<td></td>
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<td>900</td>
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<td>0.24</td>
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<td></td>
<td>1200</td>
<td>70</td>
<td>0.11</td>
<td>62</td>
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</table>
The authors found that addition of γ- Al₂O₃ improves the sinter stability of the aerogel network significantly and an admixture of only 6% of the powders reduces the shrinkage at 1000 °C by a factor of three. Cluzel et al. studied the structure of two different kinds of mullite aerogels obtained from CO₂ or methanol evacuation [61]. The thermal evolution was studied by dilatometric measurements. The temperature vs. linear shrinkage (%) is provided in Fig. 2.1.10. The linear shrinkage (%) for silica was found to be 30%, for 5 wt% alumina the shrinkage was found to be 20% and for 15 wt% alumina the shrinkage was only 20%. The shrinkage for 25 wt% alumina was found to be only 15%. This confirms that aluminium sites shield adjacent Si-OH…OH-Si groups thus preventing the dehydroxyltion and silanol condensation.

![Fig. 2.1.10. Linear shrinkage (%) of (A) Silica aerogel (B) 5 wt% (C) 15 wt% and (D) 25 wt% alumina](image-url)

*Fig. 2.1.10. Linear shrinkage (%) of (A) Silica aerogel (B) 5 wt% (C) 15 wt% and (D) 25 wt% alumina*
The total acidity for 5 wt% alumina determined via TPD measurements was found to be 2.09 mmol/g and for 10% alumina it was found to be 2.13 mmol/g. When alumina is added to silica, there will be charge imbalance since alumina is octahedral and silica is tetrahedral. Substitution of Si by Al in to tetrahedral sites of SiO$_2$ creates a charge imbalance, which can be neutralized by H$^+$ cations from water molecules, which dissociate to give hydroxyl anions on the Al$^{3+}$ cations. [53]. The total acidity for 25 wt% alumina was found to be 1.38 mmol/g and this is due to the decrease in the surface area for 25 wt% alumina aerogel.

Fig. 2.1.11. XRD spectrum of 25% alumina calcined at 1200 °C.

The X-ray analysis of 25% alumina-silica aerogel calcined at 1200 °C (Fig. 2.1.11) samples showed no peaks corresponding to $\alpha$-Al$_2$O$_3$ which suggests that the alumina in the aerogel is distributed homogeneously on a molecular scale.
2.1.5 Conclusion

A sol-gel route followed by non-supercritical drying was employed for the synthesis of silica-alumina mixed oxide aerogels. The aerogels which were calcined at different temperatures were characterised by Nitrogen sorption studies. The FTIR studies indicated the presence of Si-O-Al bonds in the mixed oxide system after calcining it at 500 °C. The resultant silica-alumina aerogel with an alumina content of 5 wt% showed a surface area of 796 m$^2$/g at 500 °C. With the incorporation of 15 and 25 wt% alumina, the thermal pore stability of silica aerogel was retained up to a temperature of 1200 °C. TMA indicated that the linear shrinkage (%) was only 15% for 25wt% alumina when compared with that of silica which had shrinkage of 30%. Temperature-programmed desorption studies revealed that the aerogels were acidic and the aerogel with 10 wt% alumina showed the highest acidity. The aerogels were homogeneous since there was no $\alpha$-Al$_2$O$_3$ peak in the XRD pattern even after calcining at 1200 °C.
2.2 Non-Supercritically Dried Silica-Alumina Aerogels-Effect of Gelation pH

2.2.1 Abstract

Silica-alumina mixed oxide aerogels having compositions containing 5, 10, 15, 20 and 25 wt% of alumina in silica have been synthesised by a hybrid sol-gel technique followed by subcritical drying. The gelation has been carried out under pH of 3 and 5. The pH is a decisive parameter which affects the rate of hydrolysis and condensation of alkoxides. Moreover it also influences the surface area and porosity features of the final material. The gelation times have been found to be much longer for the gels which were gelled at pH 3. Nitrogen sorption studies of the aerogels calcined at 500 °C indicate that the mixed oxide aerogels are mesoporous in nature and the gel prepared under a gelation pH of 3 has been found to have higher surface area than the pH 5 counterpart. Transmission Electron Microscopy (TEM) and X-ray diffraction (XRD) analysis have been performed to verify the homogeneity of the mixed oxide aerogel.

2.2.2 Introduction

Silica–Alumina mixed oxide systems have attracted considerable academic and industrial attention owing to their application as catalyst [1-6]. An attractive method to synthesise metal catalysts and mixed metal oxide catalysts is the sol-gel method [5]. One of the most investigated forms of metal oxide catalysts is the aerogels. Aerogels are normally prepared by drying under supercritical conditions of the pore fluid. Attempts to replace the conventional drying technique for the preparation of silica-alumina mixed oxide aerogels was discussed in Chapter 2 section 2.1. The success of the drying technique, choice of the alumina precursor and its thermal pore stability were reported in this chapter. The hydrolysis conditions for the reported preparation had to be maintained
in a narrow pH window to eliminate segregation limiting the structural variations that could be achieved by changing the hydrolysis conditions in the method. But on the other hand the gelation pH is also an influential parameter that determines the final structure of the material which was not discussed in our previous report. The condensation reaction leading to gelation proceeds via a base-catalysed mechanism for pH above the isoelectric point of silica (pH 2) and is acid catalysed for pH below the isoelectric point of silica [62]. A change in gelation pH is known to yield products ranging from weakly branched polymers to compact particulates [63]. A hydrolysis rate that is rapid compared with the condensation rate is expected to favour the formation of compact particulate structures [64] and it is reported that such conditions prevail under pH conditions between 2 to 4 [62]. Hence in this chapter, the effect of gelation at a pH of 3 and 5 on the structural characteristics of silica-alumina aerogels prepared by subcritical drying is discussed.

2.2.3 Experimental

Boehmite, (AlOOH) (99% purity, alumina content 70%, Condea Chemie, Germany) having BET surface area of 230 m$^2$/g and crystalline size 48-60 Å was used as the precursor for alumina and Tetraethoxysilane (TEOS) (98% purity, Fluka, Switzerland) for silica. Boehmite sol was prepared by dispersing 20 g of boehmite powder in 2 L water, by keeping under stirring while the pH was adjusted to 3.5 by addition of 20% HNO$_3$ (S.D. Fine Chemicals, India). The concentration of alumina in the stock boehmite sol was 0.0107 g/ml. For preparing silica sol, TEOS in isopropanol (S.D. Fine Chemicals, India) was hydrolysed with HCl (S.D. Fine Chemicals, India) (pH=1.54) in a molar ratio of 1: 4: 16 [18]. In a typical experiment for preparing 25 wt% alumina in silica, 3.884 g of TEOS in 4.475 g isopropanol was hydrolysed using 5.45g of H$_2$O
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(pH=1.54, HCl). The clear sol was stirred for 30 min, 35 ml boehmite was added and the sol was again stirred for 30 min. Subsequently, the gelation pH was adjusted to 5 using 5% ammonia solution. Another batch of experiment was done by changing the gelation pH to 3. The visually homogeneous sol was then transferred to vials (2cm diameter) and kept at 50 °C for gelation. The gelation time was noted. The gels were aged for 5 to 6 h and then were transferred to water taken in a beaker and was kept for 24 h at 50 °C. The gels were then soaked in isopropanol and the isopropanol was changed five times within 24 h in order to remove water from the pores. During this process the gels were kept at 50 °C. This was followed by aging the gels in 80% TEOS for 48 h at 50 °C and finally solvent exchange with isopropanol was performed at the same temperature i.e. at 50 °C. The gels were then dried in tightly closed containers at 70 °C so that the porous structure is retained in the gels by the slow removal of solvent from the pore network. The aerogels obtained after drying at 70 °C were calcined for 3 h at 500 °C. The alumina content was varied from 5 to 25 wt%. The detailed experimental Flowchart is provided in Fig. 2.2.1.

Bulk density of the dried gels was calculated from the mass and volume and the volumes were obtained from the diameter and thickness of the gel. The BET surface area of calcined aerogels were determined by N₂ adsorption at 77K (Micromeritics, Gemini Model 2360, USA). For Transmission Electron Microscopy (TEM) studies, the gel samples were dispersed in acetone. A few drops were placed on to a carbon coated copper grid. After ensuring the evaporation of the solvent, the copper grid was mounted in a FEI High Resolution Transmission electron microscope (HRTEM) Technai 30G² S-TWIN. The X-ray powder diffraction patterns of the calcined samples were recorded in
Philips Diffractometer (PW 1710), Netherlands, using Ni filtered CuKα radiation. The samples were scanned from 0 to 60° (2θ values) with a step speed of 2.4°/min.

Fig. 2.2.1. Flowchart for the preparation of Silica-Alumina mixed oxide aerogels

- TEOS + isopropanol + 0.001 M HCl
- Silica precursor sol
- Adjusting the pH to 3 and 5
- Silica-Alumina gel rods
- Aging in water for 24 hours
- Solvent exchange (isopropanol)
- Silane aging (48 hours)
- Solvent exchange (isopropanol)
- Drying at 70 °C
- Calcining at 500 °C
2.2.4 Results and Discussion

The gelation time for silica as well as those containing various alumina compositions is provided in Table 2.2.1. As the alumina content increases the gelation time gets prolonged. Huang et al. found that increase of water content (as a reactant) would increase the gel time [51]. Here the TEOS: water was kept constant at 1:16, but to obtain higher loadings of alumina, a larger volume of boehmite sol was required compared with lower alumina compositions. When more and more of boehmite sol is added, water separates the condensation product and thereby decreases condensation rates. As the gelation pH is increased from 3 to 5, the gelation time is shortened. At pH 5 the hydrolysed species are consumed much faster than at pH 3 which should favour faster condensation to a three dimensional network. In the mixed system silanol groups undergo cross condensation with boehmite particles and result in a composite network structure upon gelation, with boehmite particles serving in the formation of the skeleton by a mechanism similar to that happens when silica soot is added to hydrolysed TEOS [65].

The photograph of aerogels synthesised in the present work is provided in Fig. 2.2.2. Usually the bulk density of aerogels ranges from 0.003 to 0.8 g/cm$^3$ with high surface area extending up to about 1500 m$^2$/g [66-68]. The density measurements of the as prepared silica-alumina aerogels and pure silica aerogel prepared are provided in Table 2.2.1. The adsorption isotherms of silica and mixed-oxide aerogels gelled at pH 3 and pH 5 are provided in Fig. 2.2.3.
Fig. 2.2.2. Photograph of silica-alumina mixed oxide aerogels

Fig. 2.2.3. Adsorption isotherms of (A) silica (pH 3) (B) 5 wt% (pH 3) (C) 10 wt% (pH 3) (D) 15 wt% (pH 3) (E) 20 wt% (pH 3) (F) 25 wt% alumina (pH 3) (G) silica (pH 5) (H) 5 wt% (pH 5) (I) 10 wt% (pH 5) (J) 15 wt% (pH 5) (K) 20 wt% (pH 5) and (L) 25 wt% (pH 5) alumina
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The isotherms are Type IV which indicates that the aerogels are mesoporous. The amount of nitrogen adsorbed decreases as the percentage of alumina is increased. The decrease in the amount of nitrogen adsorbed indicates the decrease in the total pore volume and hence a decrease in the surface area. The surface area, total pore volume and pore diameter values of silica and silica-alumina mixed oxide gels prepared under gelation pH 3 and pH 5 are provided in Table 2.2.1.

F.M.A. Margaca et al. used the small angle neutron studies (SANS) to investigate the microstructure at nanoscale level, of silica gels at different processing stages [69]. The samples were prepared by the alkoxide route of the sol-gel process with different pH values. For gels prepared in strong acidic conditions, linear polymers were observed and an oxide network develops by means of a process that could be described by DLCCA (Diffusion Limited Cluster-Cluster Aggregation) model. In the case of gels produced in basic conditions, the scattering object growing in the sol has no similarity with a linear polymer and is observed to be particle like. The oxide network growth occurs through a process that can be described by the RLMCA model (Reaction Limited Monomer-Cluster Aggregation) [69]. J. Estella studied the simultaneous effect of pH, temperature, ethanol: TEOS and water: TEOS molar ratio on gelation time and textural and structural properties [70]. At pH 2.5, porous texture of gels is made up from ultramicropores, whereas at pH 4.5 porous texture is in the range of supermicropores. Tamon et al. observed that the surface area and the pore radius of the aerogels were controlled by changing the molar ratio of ammonia to TMOS in sol-gel polymerization [3]. As the ratio increases, the radius decreases. In acidic conditions TEOS rapidly undergoes hydrolysis to form triethoxy silanol species. The alkoxy groups are proton donating and when alkoxy group
is removed, protonation of this silanol species will be less favourable and the second hydrolisation step will be slower. The condensation between partially hydrolysed monomers and silanol species plays a crucial role. The terminal Si \((\text{OC}_2\text{H}_5)\) is reactive because of steric and inductive reasons and hence acid catalysed hydrolisation will lead to chain elongation and thereby formation of linear polymers \([63, 69]\). The entanglement of these linear polymers leads to dense gels with small pores \([70]\). This effect will be more marked for pH 3 than for pH 5. When pH is higher, condensation is faster when compared at pH 3 and the reaction at the central silicon atom of an oligomer is favoured. So the resulting network is characterised by big particles and large pores \([67]\). The aerogels which are prepared at a gelation pH of 3 have a higher surface area than the ones which are prepared at a gelation pH 5 which is due to fact that pH 3 gelled aerogels have larger pore volume compared to pH 5 gelled ones.

Transmission Electron Microscopy (TEM) studies confirmed that the prepared aerogel is meso/macro porous with a network structure. The Bright field TEM image of 5 wt% alumina-silica calcined at 500 °C (pH 5) (Fig. 2.2.3) and 25 wt% alumina-Silica aerogel calcined at 500 °C (pH 5) (Fig. 2.2.4) apparently exhibited meso-/macro-porous structure. The lighter area in the TEM is the several nanometer-sized pores. The selected area diffraction pattern (Fig. 2.2.3 and Fig. 2.2.4 inset- Top left) of 5% alumina calcined at 500 °C (pH 5) and 25 wt% alumina calcined at 500 °C (pH 5) indicates that the aerogel is amorphous. The elemental analysis employing EDAX of 5wt% alumina-silica calcined at 500 °C (pH 5) (Fig. 2.2.3. inset- Top right) and 25 wt% alumina-Silica aerogel calcined at 500 °C (pH 5) (Fig. 2.2.4 inset- Bottom right) shows the presence of Al. The silanol groups undergo cross condensation with boehmite particles and on
subsequent calcination, it will lead to the formation of Si-O-Al bonds. The Si-O-Al bond formation starts from 400 °C and the samples are calcined at 500 °C.

Table 2.2.1. Surface area and pore volume of silica and silica-alumina aerogels prepared under gelation pH of 3 and 5 and calcined at 500 °C.

<table>
<thead>
<tr>
<th>Alumina content in mixed oxide Sol (wt %)</th>
<th>Gelation pH</th>
<th>Gelation time (min)</th>
<th>Density (g/cm³)</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 3</td>
<td>0</td>
<td>480</td>
<td>0.34</td>
<td>794</td>
<td>1.266</td>
<td>58</td>
</tr>
<tr>
<td>pH 5</td>
<td></td>
<td>14</td>
<td>0.401</td>
<td>736</td>
<td>1.23</td>
<td>66</td>
</tr>
<tr>
<td>pH 3</td>
<td>5</td>
<td>960</td>
<td>0.423</td>
<td>744</td>
<td>1.3</td>
<td>51</td>
</tr>
<tr>
<td>pH 5</td>
<td></td>
<td>25</td>
<td>0.400</td>
<td>796</td>
<td>0.94</td>
<td>65</td>
</tr>
<tr>
<td>pH 3</td>
<td>10</td>
<td>1875</td>
<td>0.516</td>
<td>676</td>
<td>1.18</td>
<td>65</td>
</tr>
<tr>
<td>pH 5</td>
<td></td>
<td>70</td>
<td>0.54</td>
<td>618</td>
<td>1.09</td>
<td>69</td>
</tr>
<tr>
<td>pH 3</td>
<td>15</td>
<td>3300</td>
<td>0.65</td>
<td>506</td>
<td>0.74</td>
<td>49</td>
</tr>
<tr>
<td>pH 5</td>
<td></td>
<td>110</td>
<td>0.63</td>
<td>420</td>
<td>0.57</td>
<td>53</td>
</tr>
<tr>
<td>pH 3</td>
<td>20</td>
<td>3840</td>
<td>Cracked gel</td>
<td>422</td>
<td>0.59</td>
<td>53</td>
</tr>
<tr>
<td>pH 5</td>
<td></td>
<td>150</td>
<td>Cracked gel</td>
<td>272</td>
<td>0.34</td>
<td>57</td>
</tr>
<tr>
<td>pH 3</td>
<td>25</td>
<td>4800</td>
<td>Cracked gel</td>
<td>390</td>
<td>0.37</td>
<td>38</td>
</tr>
<tr>
<td>pH 5</td>
<td></td>
<td>220</td>
<td>Cracked gel</td>
<td>266</td>
<td>0.33</td>
<td>49</td>
</tr>
</tbody>
</table>
Fig. 2.2.3. Bright Field image of 5 wt% alumina aerogel calcined at 500 °C (pH 5), Selected area diffraction pattern of (Inset-Top left) and EDAX spectrum (Inset-Top right) of 5 wt% alumina aerogel.

Moreover Si-O-Al bond formation is a direct reflection of the structural homogeneity of the aerogel. The absence of any crystalline phase, particularly $\alpha$-alumina on calcination at 1200 °C, indicates that boehmite particles are homogeneously distributed throughout the aerogel without any segregation in the nanoscale.
Fig. 2.2.4. Bright Field image of 25 wt% alumina aerogel calcined at 500 °C (pH 5), selected area diffraction pattern (Inset-Top left) and EDAX spectrum (Inset-Bottom right) of 25 wt% alumina aerogel.

2.2.5 Conclusion

A hybrid sol-gel route followed by subcritical drying was employed for the synthesis of silica-alumina mixed oxide aerogels. The gelation was carried out under pH of 3 and 5. The aerogels which were prepared by gelation at pH 3 had a higher surface area than the ones which were prepared at gelation pH 5. The reduction in surface area is attributed to the formation of larger pores. TEM microstructural analysis indicates that the aerogel is amorphous and absence of $\alpha$-Al$_2$O$_3$ even after calcination at 1200 °C, is a direct consequence of alumina being homogeneously dispersed in the silica network which was confirmed using X-ray diffraction.
References


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