

Synthesis and Some Physical Features of Silica Xerogels Derived by Sol-Gel Method

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Abstract: This paper is concerned about the synthesis of silica xerogel samples at different values of pH by using inexpensive silica precursor (Na_2SiO_3). The synthesized xerogels were tested for physical tests like Scanning Electron Microscopy (SEM), X-rays diffractions (XRD) and Fourier Transform Infrared (FTIR) Spectroscopy. The micrographs of the gel obtained at higher pH values of the precursor solution showed that the particles are glassy and shiny in appearance. In the X-rays diffractogram of the gel sample where 6 % sodium silicate was used displayed only a single peak at $2\theta = 74^\circ$ which points towards the crystalline nature of the sample. However, the xerogel with 4 % of the silica precursor showed no peak except a broad peak centered at 2θ angle of 22° which confirmed its amorphous nature. The crystallinity was observed to be affected with the change in pH of the precursor during the gel fabrication.

Key Words: Characterization; Spectroscopy; Sodium silicate; Silica xerogel; Scanning electron microscopy; X-rays diffraction.

Introduction

Silica xerogel due to comparatively less reactive nature has been considered as a suitable material for a variety of applications. A xerogel is formed by drying a gel at room temperature and pressure. In the fabrication of silica xerogel, pH was reported to be a critical parameter in determining its quality [1]. The xerogel maintains enormous porosity (25%) and high surface area (150-900 m^2/g); along with narrow average pore size (1-10 nm). However, during the evaporation of solvent, their structure collapses and the size shrinks because of capillary action. The combination of a wide range of unusual properties enables xerogels to seek the applications in various sectors. The xerogels can be used as adsorbent for pollutants as well as due to chemically inert nature these gels are suggested to be a good carrier for the drugs and other active chemical and biochemical species [2]. Further, by varying the reaction conditions and the nature of precursors or additives, different varieties of xerogels can be prepared and henceforth can find applications in separations, biomedicine, glazing, paints, sensors, thermal insulation, catalyst carriers and oil spill clean-up [3-7].

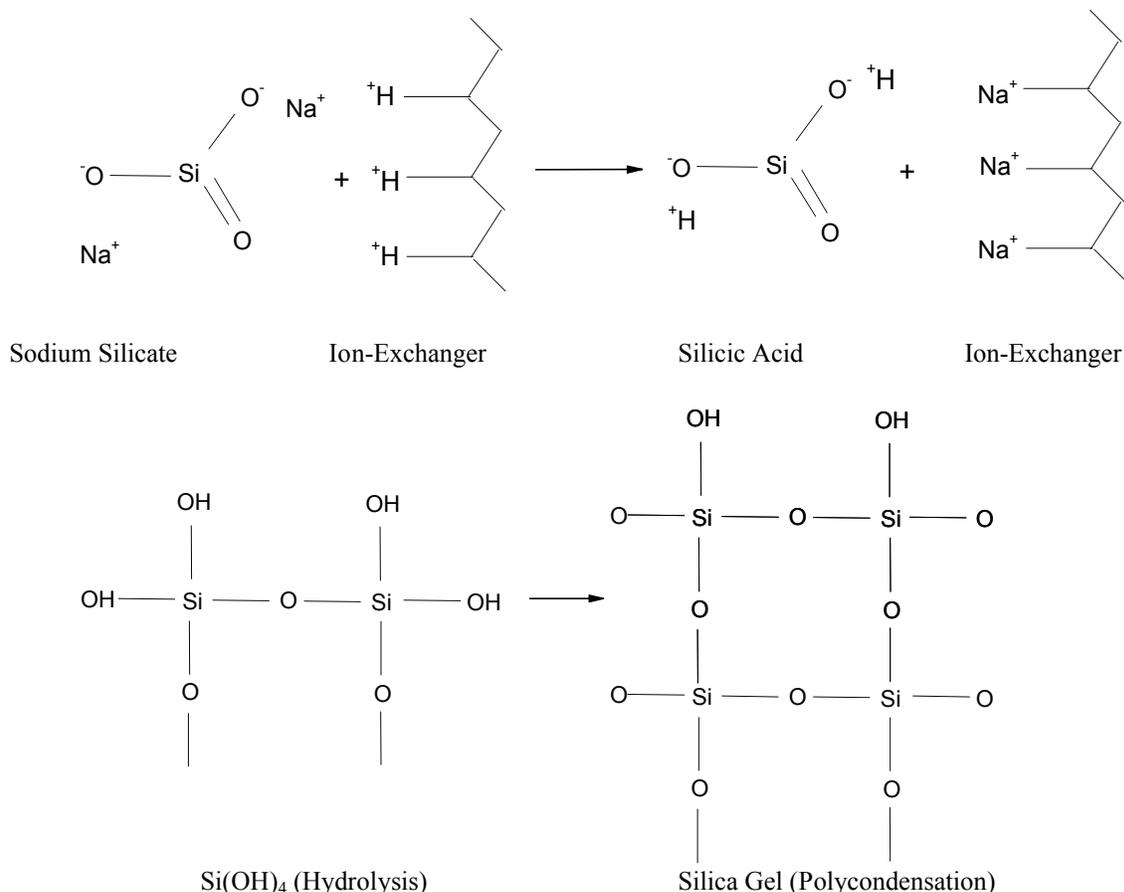
The sol-gel encompasses the shift of a system from a colloidal into a solid gel phase [8]. Several kinds of low molecular weight alkoxides such as tetraethoxysilane (TEOS), tetramethoxysilane

(TMOS) and sodium silicate are mostly used as silica precursors. In sol-gel process, the precursor material is applied to a sequence of hydrolysis and polycondensation reactions to form a colloidal suspension, named as *sol* [9]. Further, this process permits one to design and fabricate the ceramic materials in different forms and even thin film can be formed by the process of either spin-coating or dip-coating.

The present study deals with the synthesis of silica xerogel samples by sol-gel method. The xerogel will be characterized for various analytical tests. Ion exchange method will be adopted for the preparation of samples. During the preparation, 4 and 6 % sodium silicate will be used as silica precursor. Scheme 1 will be adopted for the preparation of silica xerogel.

Sodium silicate during the exchange reactions with a cation exchanger (Amberlite IR-2000) resulted in the formation of silicic acid which upon hydrolysis gives $\text{Si}(\text{OH})_4$. Finally, polycondensation will result in the formation of Si – O – Si network.

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Scheme-1: Formation of silicic acid via ion exchange mechanism.

Experimental

Materials and Methods

Sodium silicate was acquired from Sigma Aldrich. Ammonium hydroxide was provided by Fischer Scientific while Amberlite IR 2000 was supplied by Merck. All the chemicals were used as received and their solutions were prepared in deionized water.

Synthesis of Xerogels

Sodium silicate (4 and 6 %) solution was prepared in deionized water. The solution was gradually delivered through the ion-exchanger (Amberlite IR-2000) packed in a 25 inch long column of 2 inches diameter and was collected in a polypropylene beaker. The pH of collected silicic acid was noted. Afterward, ammonium hydroxide (0.05 M) solution was gradually added with continuous stirring till we achieve the gel at desired pH value. The silica sol was allowed to stir for about half an hour and was then kept at 50 °C for one more

hour. Afterwards, it was kept at room temperature (covered with aluminum foil) so that the gelation proceeds smoothly. To strengthen the Si – O – Si network, the gel thus obtained was aged for 2 days. Afterward, the solvent was exchanged with deionized water. The gel powder was then stored in polythene bottles after drying at 65 °C. Table-1 shows the xerogel samples synthesized in the present work. Finally, the ion-exchanger was regenerated by washing first with 5% solution of NaOH, then with 5% HCl solution and finally with deionized water.

Table-1: Effect of pH and % solution of sodium silicate on the formation of silica xerogel.

Sample	% solution (Na ₂ SiO ₃)	pH (silicic acid)	pH (basic) (0.05 M NH ₄ OH)
1	4	2.41	2.71
2	4	2.41	3.50
3	4	2.41	4.21
4	6	2.70	5.07
5	6	2.70	6.01

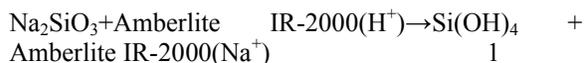
Instruments Used and Analytical Conditions

X-ray diffraction is the measurement of average space between two rows of atoms. It defines

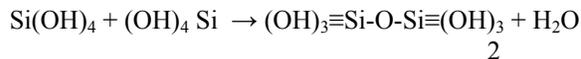
the positioning of single atom or grain and also the shape, size and internal stress of small crystalline region. The crystal morphology of gel samples are performed in X-rays diffraction model X Pert Pro (Panalytical). The source for X-rays generation was copper (1.54 Å) at 40 KV voltage and the current of 30 mA. The micrographs of samples were acquired in SEM model Hitachi-Su1500 at the operating voltage of 5 KV. The IR spectra were recorded with FTIR spectrophotometer model Nicolet 560 (transmittance mode) at room temperature. All the samples were scanned from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1} . The spectra were collected after an average of 32 scans for each sample and the data was acquired through OMNIC software.

Results and Discussion

In present manuscript silica xerogels were synthesized from silicic acid at desired pH values as show Table 1. During the ion exchange process, the positively charged Na^+ ions of sodium silicate are replaced with smaller and more mobile H^+ ions of the ion exchanger resulting in the formation of silicic acid. With the passage of time, the pH of silicic acid thus formed will be reduced from 13.00 from to 3.0 and it condenses to form the silica gel. To accelerate the growth of gel, hydrochloric acid was used which will act as a catalyst. Finally ammonium hydroxide solution was used to assist the condensation of H_2SiO_3 to silica. The process of condensation and gelation will ensure the strengthening of Si-O-Si network in silica gel. The overall mechanism which governs can be represented in the following two equations.



The silicic acid will first condenses to form silica particles of smaller sizes and then consequently Si-O-Si network will grow due to the process of polycondensation



Scanning Electron Microscopy of Xerogels

Scanning electron micrographs of the xerogels prepared from the sodium silicate precursor are represented by Figs. 1 and 2. The SEM micrograph (A) represents the sample synthesized at pH value 2.71, whereas (B) and (C) represents the xerogels prepared at pH values 3.50 and 4.21 respectively (Fig. 1). In all these samples the concentration of sodium silicate used was 4 %. Fig. 2 represents the micrographs of the xerogels prepared at pH 5.07 and 6.01. In these samples 6 % Na_2SiO_3 was used as a silica precursor. The micrographs of the gels show that the particles have no regular shape; while are distinguishable from each other. The surface structure has also been affected with the pH of precursor solution. An increase in the pH of the xerogel precursory mixture, generally results a decreased in particle and pore sizes. The pH domains in the present work are lying close to the isoelectric point of silica [10, 11]; therefore, the impact of solution pH on the sample morphology cannot be overlooked. Further, there are chances for the faster hydrolysis and slower condensation, therefore; hydrolysis rate is enhanced at lower pH values. This resulted in the formation of larger voids surrounding more interconnected particles [12]. Further, the particles in the xerogel samples synthesized at pH 5.07 and 6.01 are better in visibility and are having glassy appearance.

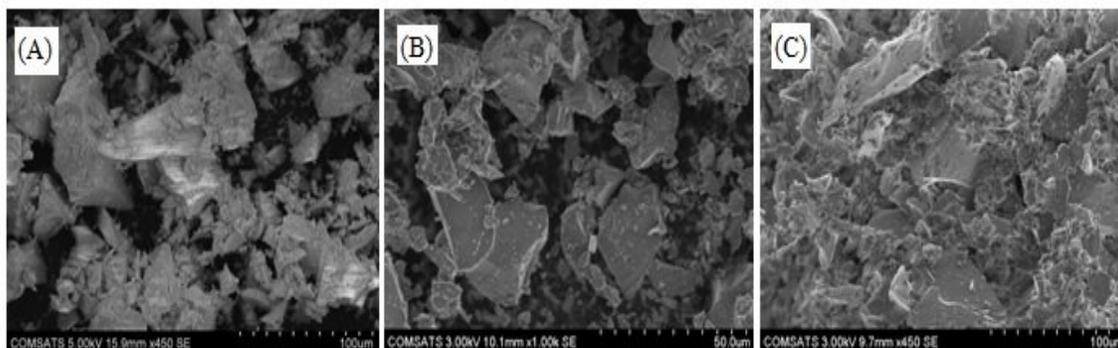


Fig. 1 SEM micrographs of xerogels synthesized at pH (A) 2.71 (B) 3.50 (C) 4.21.

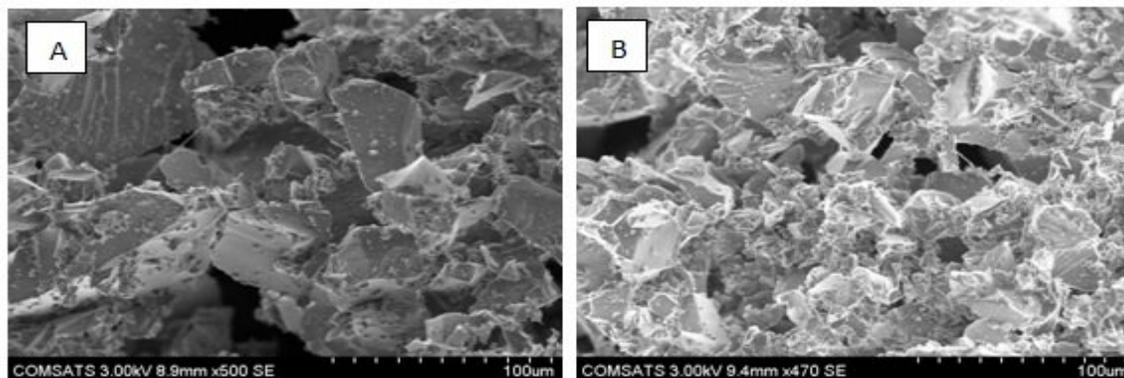


Fig. 2 SEM micrographs of xerogels synthesized at pH (A) 5.07 and (B) 6.01.

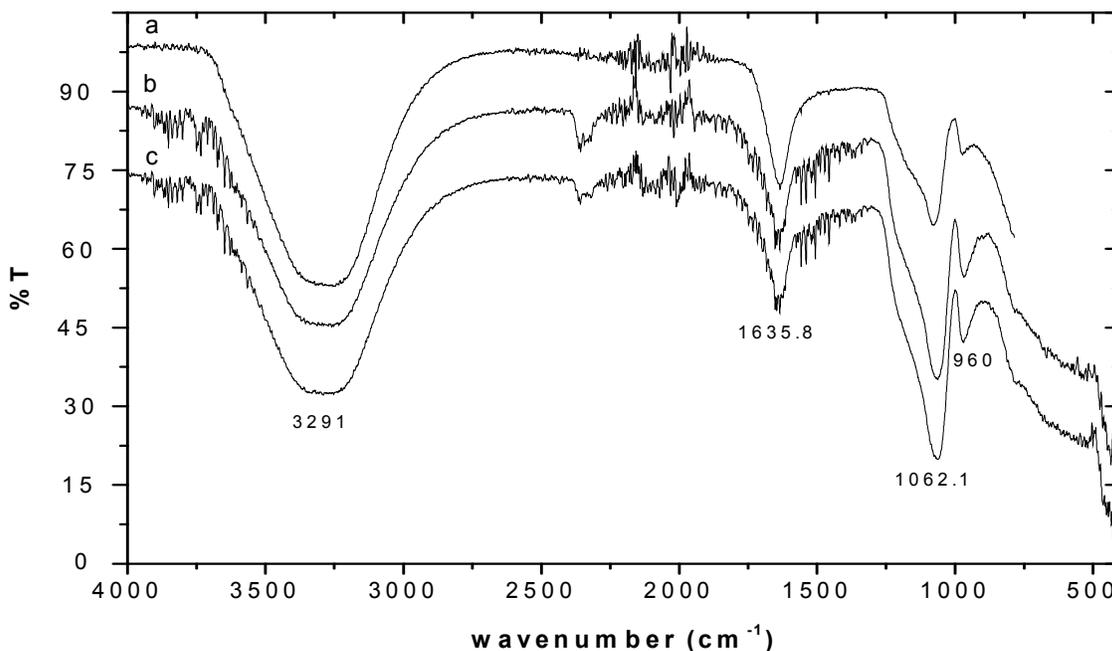


Fig. 3 FTIR spectra of xerogels synthesized at pH (A) 2.71, (B) 4.21 and (C) 6.01.

FTIR Spectroscopy of Xerogels

FTIR spectroscopy has been applied to find out the functional groups on the surface of gels. By using this spectroscopic technique, the formation of the silica xerogels skeleton structure was confirmed. The IR spectra are represented in the Fig. 3. In this Fig (A) represents the sample synthesized at pH value 2.71 while (B) represents the xerogel prepared at pH value 4.21. These spectra are related to the samples having 4 % sodium silicate. On the other hand, Fig. 3 (C) represents the spectrum of the xerogel prepared at pH 6.01 where 6 % Na_2SiO_3 was used as a silica precursor. The FTIR spectrum shows the characteristic band at 3291.0 cm^{-1} which is associated to the interactions between surface OH groups and water presented in the neighboring atmosphere. This characteristic band can be related to

the presence of isolated groups (Si-OH) and O-H stretching band, caused by the linkage of hydrogen to water molecules (H-O-H ...H) and hydrogen atom of surface silanol attached to the molecular water (Si-O-H...H₂O) [13]. The other representative bands positioned at 1062.1 cm^{-1} and 1635.8 cm^{-1} which endorse the presence of silica are directly related to the interaction of silanol groups (Si-OH) [14]. The intensity of absorption peak at 960 cm^{-1} which arises from the Si-O stretch of silanol groups increases when the gelation pH was increased from 2.71 to 4.21 and 6.01. Similarly the band intensity appeared at 1062.1 cm^{-1} which can be related to the antisymmetric stretching vibration of Si-O-Si was increased in the spectra of the gels prepared at higher pH values [15]. From FTIR studies, it can be infer that the increase in the gelation pH promotes the SiO and Si-O-Si linkages due to polycondensation.

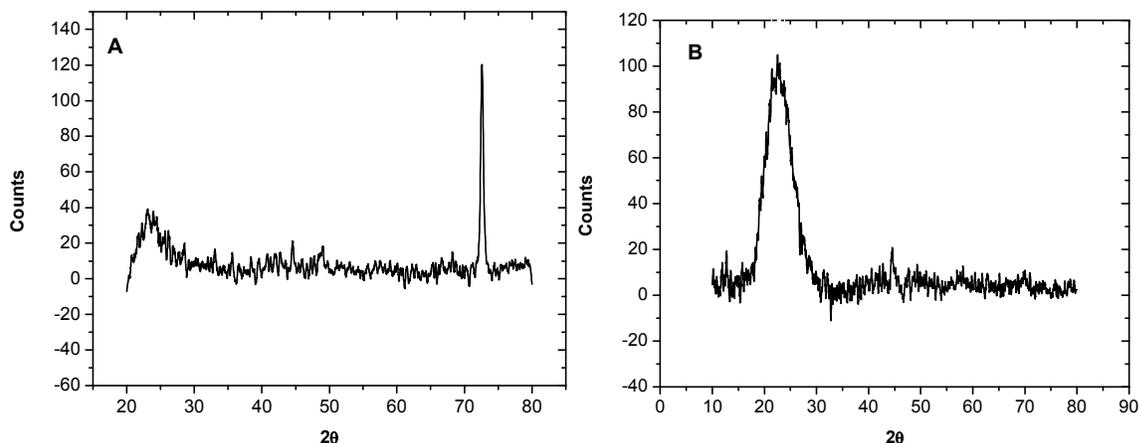


Fig. 4 X-rays diffractograms of xerogels synthesized at pH (A) 2.71 and (B) 5.07.

X-rays Diffraction Analysis of Xerogels

To find out the crystallinity of the xerogels, XRD has been applied and the diffractograms are displayed by the Fig. 4. The XRD analysis of this silica xerogel was performed by using Scherer equation in the form, $D = k\lambda/B\cos\theta$, where the shape factor k is equal to 0.89, θ is the Bragg diffraction angle, λ is the wavelength of X-rays having value equal to 1.5418 Å and B is the full width of the observed peak at half maximum (FWHM). From X-ray diffraction studies, the amorphous character of most of the studied silica xerogels was confirmed. The xerogel sample at pH 2.71 where 6 % sodium silicate was used, displayed a peak around at $2\theta = 74^\circ$ (Fig. 4 A). The hkl value was 313 and the $d_{\text{experimental}}$ value was matched with the reference card of silica xerogel with reference code, 00-004-0379. An example of amorphous xerogel was shown in the Fig. 4 (B). This gel sample was having 4 % sodium silicate which was synthesized at pH 6.01. The X-rays diffractograms of silica xerogels showed no peak except a broad peak appeared at $2\theta = 22^\circ$ which confirmed the amorphous nature of the gel. This characteristic broad peak becomes more prominent in the gel sample synthesized at higher pH values.

Conclusions

The X-rays diffraction analysis showed that the fabrication of crystalline samples of xerogels at lower pH values. All the characteristics bands thus appeared were confirmed by FTIR spectroscopy. The micrographs of the gels showed that the particles have no regular shape and their surface structure might be affected with the pH of precursor solution. Generally there is a decrease in the particle size with increasing the pH of the xerogel precursor; however, the impact of pH on the sample morphology cannot

be overlooked because the solution pH was close to IEP. It was concluded that the formation of larger voids was due to hydrolysis at lower pH values. Further, the visibility of particles was enhanced by increasing the pH of solution.

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