



Review Article

Rice Husk Ash as a Renewable Source for the Production of Value Added Silica Gel and its Application: An Overview

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Abstract

In recent years, silica gels have developed a lot of interest due to their extraordinary properties and their existing and potential applications in science and technology. Silica gel has a wide range of applications such as a desiccant, as a preservation tool to control humidity, as an adsorbent, as a catalyst and as a catalyst support. Silica gel is a rigid three-dimensional network of colloidal silica, and is classified as: aqua-gel, alco-gel, xero-gel and aero-gel. Out of all known solid porous materials, aero-gels are particularly known for their high specific surface area, high porosity, low bulk density, high thermal insulation value, ultra low dielectric constant and low index of refraction. Because of these extraordinary properties silica aero-gel has many commercial applications such as thermal window insulation, acoustic barriers, super-capacitors and catalytic supports. However, monolithic silica aero-gel has been used extensively in high energy physics in Cherenkov radiation detectors and in shock wave studies at high pressures, inertial confinement fusion (ICF) radio-luminescent and micrometeorites. Silica gel can be prepared by using various sol gel precursors but the rice husk (RH) is considered as the cheapest source for silica gel production. Rice husk is a waste product abundantly available in rice producing countries during milling of rice. This review article aims at summarizing the developments carried out so far in synthesis, properties, characterization and method of determination of silica, silica gel, silica aero-gel and silica xero-gel. The effect of synthesis parameters such as pH, temperature of burning the rice husk, acid leaching prior to formation of rice husk ash (RHA) on the properties of final product are also described. The attention is also paid on the application of RH, RHA, silica, silica aero-gel and silica xero-gel. Development of economically viable processes for getting rice husk silica with specific properties assumes importance at this juncture. Copyright © 2012 by BCREC UNDIP. All rights reserved.

Keywords: Rice husk, Rice husk ash, Sodium silicate, Silica gel, Review

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1. Introduction

Rice husk (RH) is one of the by-products obtained during milling of rice. This surrounds the paddy grain. It is reported that approximately 0.23 tons of rice husk (rice hull) is formed from every ton of rice produced [1]. World rice production is approximately 645 million tons. Asian farmers produce rice about 90% of total production of 100,000 tons or more, with two countries, China and India, growing more than half of the total crop [2]. In certain countries, it is sometimes used as a fuel for parboiling paddy in the rice mills and to power steam engines. The partially burnt rice husk in turn contributes to environmental pollution. It would be beneficial to the environment to recycle the waste to produce eco-material having high end value [3]. End use of any material including wastes depends on its structure, properties and mainly on chemical composition. Chemical compositions of rice husk vary from sample to sample. This variation is due to differences in climatic and geographical conditions, type of paddy etc [4-6]. The chemical analysis of rice husk is shown in Table 1. SiO₂ is found to be 22.12%, the organic material and water content is 74% and (Al₂O₃+Fe₂O₃+CaO+MgO) constitute about 4%. The percentage of SiO₂ varies from 15 to 22%.

Sharma et al., [5] analyzed all the reported data on organic constituents of rice husk after excluding silica and gave an average composition as given in the Table 2. The organic part is

composed of cellulose, lignin and hemicellulose; the latter is a mixture of D-xylose, L-arabinose, methylglucuronic acid and D-galactose.

1.1. Components and Structure of Rice Husk

It is generally reported that in rice husk, silica is predominantly in inorganic linkages, but some of the silica is also bonded covalently to the organic compounds. This portion of the silica is undissolved in alkali and can withstand very high temperatures [7]. It has been cleared that once the organic part of RH is extracted, the inorganic residue may be relatively pure, forming a better source for silica. Characterizations by Scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDX) etc., suggest that silica is present all over, but is concentrated on protuberances and hairs (trichomes) on the outer epidermis, adjacent to the rice kernel [5, 8,9].

There is a significant variation in silica percentage. The silica is in hydrated amorphous form, either opal or silica gel. Figure 1 shows the SEM photographs of RH and Figure 2 clearly shows the protuberances and silica [10].

1.2. Uses of Rice Husk

A number of rice-producing countries including India are currently conducting research on industrial uses of rice husk. Some of the current

Table 1. Chemical analysis of raw rice husk [5]

Constituent	Content (wt %)
Organic material and moisture	73.87
Al ₂ O ₃	1.23
Fe ₂ O ₃	1.28
CaO	1.24
MgO	0.21
SiO ₂	22.12
MnO ₂	0.074

Table 2. Organic constituents of RH excluding silica [5]

Constituent	Amount present in RH (wt %)
α -cellulose	43.30
Lignin	22.00
D-xylose	17.52
L-arabinose	6.53
Methylglucuronic acid	3.27
D-galactose	2.35
Total	94.99



Figure 1. SEM of rice husk showing fibrous nature [10]

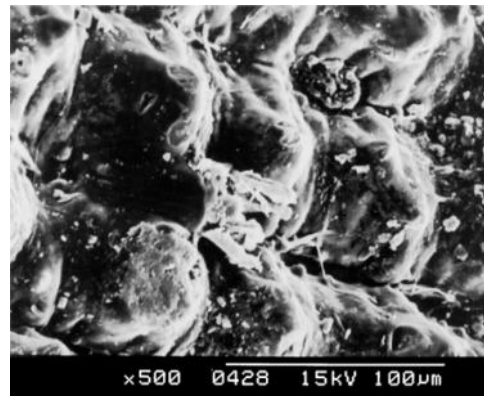


Figure 2. SEM of rice husk showing protuberance outer epidermis and silica [10]

and potential applications in various fields are listed below:

- Non energy applications
- Incorporation in soil for composting
- Bio-fertilizer additive
- Animal husbandry low quality feed
- Sorbent material in environmental remediation
- Building material with good thermal insulation
- Pest control agent
- Board manufacturing
- Composted manure

Energy generation:

- Combustion: Heat generation, cook stoves, furnaces for heating the air in rice dryers, brick kilns, etc.
- Gasification: Gas for cook stoves, Syngas for chemicals and electricity generation.
- Pyrolysis: In research phase few commercial applications.

Burning rice husk as fuel to generate energy gives a waste product rice husk ash (RHA). About 20 million tones of RHA are produced annually in India. The fibrous nature and the small grains in RH do not seem to be disturbed by burning as shown in SEM of RHA (Figure 3) [11]. Chemical composition of rice husk ash is somewhat different from that of rice husk. Percentage of silica in rice husk ash increases up to 80%. Ismail and Waliuddin has analyzed [12] the chemical composition of rice husk ash as given in the Table 3.

1.3. Uses of Rice husk ash

RHA has been used in various fields like an adsorbent, as an insulator and other application of

Table 3. Chemical analysis of rice husk ash [12]

Constituent	Amount present in rice husk ash (wt %)
Silica (SiO ₂)	80
Alumina (Al ₂ O ₃)	3.93
Sulfur trioxide (SO ₃)	0.78
Iron oxide (Fe ₂ O ₃)	0.41
Calcium oxide (CaO)	3.84
Magnesium oxide (MgO)	0.25
Sodium oxide (Na ₂ O)	0.67
Potassium oxide (K ₂ O)	1.45
Loss on ignition at 850 °C	8.56

RHA [13,14] is illustrated in Table 4.

1.4. Silica from rice husk ash

Amorphous silica powder is basic raw material used in industries associated with rubber, ceramics, electronics, catalysis, pharmaceuticals, dental material and other materials [15]. When RH is burnt in air, it leads to the formation of silica ash, which varies from gray to black depending upon inorganic impurities and unburnt carbon amount [16]. RHA can be obtained by burning rice husk in electric furnace at 600 °C for 4 hours [17]. Another study reported [18] that burning of RH (–10 mm) in a fluidized bed of fine sand (0.5mm diameter) with cross section of 380×406 mm and total height of 4.8 m. The bed temperature is maintained at 923–1173 K, fluidizing velocity is kept 0.4–2.2 m/s, bed depth is 30–60 cm and excess air levels of 30–95%. A proto type incinerator was designed with special features to burn rice husk

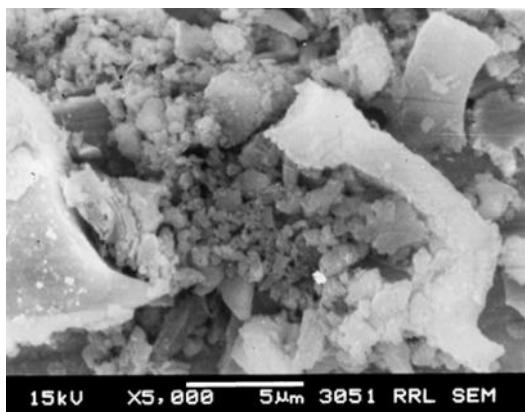


Figure 3. SEM of white ash of RH [11].

and produce amorphous and highly reactive silica [19]:

- Pure silica can be obtained from RHA by various procedures:
- Fluidized bed [20]
- Chemical pre and post treatment using acid and base solution [2]
- Pressurized hot water treatment processes [21]
- Carbonization and combustion [22]
- Non isothermal decomposition in oxidizing atmosphere [23]

A low energy method to produce pure silica (93% with 2.6% moisture) from RHA with 91% yield was developed by Kalapathy et al., [2000]. Pure silica is obtained by dissolving RHA silica with alkali solution to form sodium silicate solution and subsequently forming silica aqua-gel by adding HCl to lower the pH from 11.8 to 7.0 followed by washing and drying to get pure silica [24]. Shelke et al. produced silica from RHA as sodium silicate source using aqueous sodium hydroxide. Silica was precipitated from sodium silicate by acidification using orthophosphoric acid. The addition of the acid was done very slowly till a pH of 6.5 was reached. A precipitate of white silica was obtained. The wet precipitate was dried in an oven for 24 h at 110 °C. Silica obtained was in form of white amorphous powder having purity 98 %, bulk density 1.25 g/ml [25].

2. Effect of temperature on burning of rice husk

2.1 Amorphous and Crystalline silica

On burning rice husk, ash containing a very high percentage of crystalline silica is formed. However, if RH is burnt under controlled conditions, highly reactive amorphous silica is

Table 4. Uses of Rice husk ash [4,13,14]

Feature	Application
Absorbent	For oils and chemicals [13, 14]
Insulator	<ul style="list-style-type: none"> • As insulation powder in steel mills • In homes and refrigerants • In the manufacture of refractory bricks
Release agent	As a release agent in the ceramics industry
Pozzolan	<ul style="list-style-type: none"> • Cement industry • Concrete industry
Repellents	As repellents in the form of "vinegar-tar"
Aggregates and fillers	Aggregates and fillers for concrete
Soil ameliorant	Soil ameliorant to help break up clay soils and improve soil structure
Source of silicon	Manufacture of industrial chemicals like silica, sodium silicate, zeolite and refractory material such as SiC, Si ₃ N ₄ [4]
Substitute for micro silica / silica fumes	RHA can also replace silica fume in high strength concrete
Water purifier	To filter arsenic from water
As a vulcanizing agent	Vulcanizing agent for ethylene-propylene-dieneterpolymer (EPDM)

produced. It is observed that the ash formed at lower temperatures (773–873 K) consist of amorphous silica. Amorphous silica is one of the industrial white minerals along with china clay, CaCO₃ and talc, which are used as filler in paper, paint, rubber, fertilizers and insecticides. Amorphous silica having high purity, small particle size and high surface area can be of use as an adsorbent or catalyst support in fine chemical synthesis. In order to prepare amorphous silica with high purity from rice husk, either thermal treatment [6] of the husk or treatment with various chemicals was attempted [2, 26] before and after combustion at temperatures ranging from 773 to 1673 K for different intervals of time. The chemicals included are HCl, H₂SO₄, HNO₃, NaOH, NH₄OH, etc.

Table 5. Physical properties of silica gel [3, 37]

Property	Value	Comments
Thermal conductivity	~0.01 W/m.K	Determined by Vacuum Insulation Conductivity Tester
Bulk density	0.45 g/ml	Determined by using Helium pincometry
Porosity	80%	Determined by BET method
Specific surface area	142-357m ² /g	Determined by nitrogen adsorption/desorption
Mean pore diameter	~13nm	Determined by nitrogen adsorption/desorption
Primary particle diameter	5-50nm	Determined by electron microscopy
Refractive index	1.46	Very low for a solid material
Dielectric constant	~1-2	Very low for a solid material

The crystalline forms cristobalite and tridymite were detected at temperature >1073 K and >1423 K respectively [27]. Crystallization of silica has to be prevented by controlling the temperature and time of burning so that maximum amorphous variety is produced. Patel et al. [6] reported that the temperature of carbonization is preferably held below 973 K to avoid any transformation of the amorphous phase to a crystalline form. It has been found that reheating the ash to remove carbon residues takes a relatively long period of time and somewhat higher temperatures, with the consequence that any amorphous silica is then converted to a crystalline form.

2.2. Combustion of rice husk after leaching with acid

It is analyzed by many authors [28] that preliminary leaching of rice husk with solution of HCl, HNO₃, H₂SO₄, NaOH, NH₄OH, boiled before thermal treatment with temperature ranging from 500-1400 °C, for various time intervals [16,29] is effective in removing most of the metallic impurities and produces ash silica completely white in color with a high specific surface area. The ash from complete combustion of acid treated husk was white whereas that from the untreated husk under same conditions gave light brown product [30]. The acid treatment of rice husk did not affect the amorphousness of the silica. Real et al. [28]

found that the preliminary leaching of RH with a solution of HCl before combustion at 600 °C could result in relatively pure silica (approximately 99.5%) with a high specific surface area (approximately 260 m²/g). If the leaching with HCl was performed on the white ashes obtained from the combustion of RH at 600 °C, amorphous silica with the same purity was also obtained, but its specific surface area decreased to 1 m²/g. The formation of black particles in the silica from untreated husk was found higher than that from acid treated husk. Potassium in the husk is responsible to cause this phenomenon, which is removed to a great extent by acid treatment [16]. Pre treatment of rice husk with HNO₃ and calcination at 873 K is reported to give white, amorphous and chemically pure silica (98.5%). Other acids like sulfuric, oxalic, and citric acids can also be used for leaching of rice husk but experimental results show that silica produced by hydrochloric acid possesses higher surface area than that of sulfuric, oxalic, and citric acids [31].

3. Silica gel

Silica gels can be prepared by the sol-gel method using a variety of starting materials as the silicon source, for example:

- Rice husk ash [32,33]
- Sodium silicate [34]

Tetraethylorthosilicate (TEOS) [33-36]. SiO₂ gel made from TEOS is more expensive than that made from rice husk ash and additionally TEOS is a hazardous chemical. Further, utilization of waste rice husk ash is very attractive as value added product of silica gel.

RHA gives a yield of 73.10% means 10 g of it can produce 7.31 g of silica gel [3]. However the structure of silica present in the ash treated at 700 °C for 6 h remained essentially amorphous [27]. Typical properties of silica gel are shown below in Table 5.

3.1. Classification of silica gel

Silica gel is a rigid three-dimensional network of colloidal silica, and is classified as:

- Aqua-gel (pores are filled with water)
- Xero-gel (aqueous phase in the pores is removed by evaporation)
- Aero-gel (solvent is removed by supercritical extraction)

3.2. Preparation of silica gel

Several researchers [3, 37, 38] prepared various types of silica gels using RHA following different

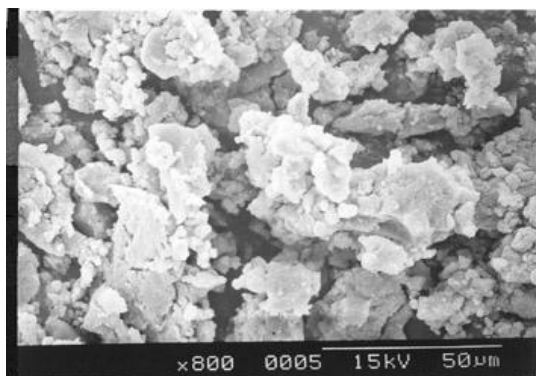


Figure 4. SEM of silica gel obtained from RHA [37]

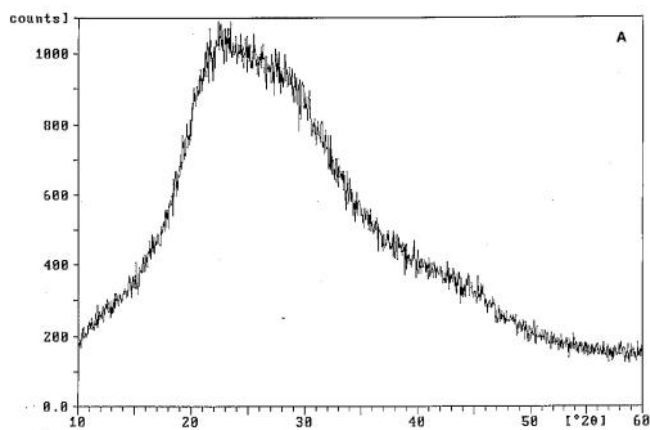


Figure 5. X-ray diffraction patterns for rice husk silica gel [37]

procedures as summarized below.

Kamath et al. [37] prepared silica gel from RHA using 1M sulfuric acid at pH 7. Prepared silica gel was aged, washed, and dried under specific conditions to get a final product that was slightly basic and had a moisture content >65%. The surface area obtained was 258 m²/g, the particle pore diameter was 12.1 nm. Scanning electron micrographs revealed that rice husk silica gel particles ranged in sizes from 5-40 nm. SEM and XRD pattern of silica gel obtained are shown in the Figure 4 and in Figure 5 respectively.

A lot of improvements have done in the preparation of silica gel from rice husk. Pijarn et al. [3] prepared silica gel by the following procedure. A mixture of rice husk ash (10 g) calcined at 650 °C for 6 h and 1 M NaOH (320 cm³) was heated under reflux for 3, 5 and 9 h. The reaction mixture was filtered via a Whatman filter paper under vacuum. Carbon residue was washed in boiled water filter (200 or 400 cm³). The filtrate, a sodium silicate solution, was cooled to room temperature and slowly titrated against 1 M H₂SO₄ with constant stirring. The pH of the solution was monitored and the titration stopped once the pH reached 7. When the gel formed from the sol, it was aged for 18 h. After aging, the gel was gently broken and the slurry was centrifuged for 5 min at 6000 rpm. Distilled water (400 cm³) was added to the gel, and the mixture gently swirled and centrifuged. The washing step was repeated 2 to 8 times. Subsequently, the gel was spread on a glass dish and dried in a vacuum oven at 80 °C. The agglomerated silica gel was then ball-milled using ZrO₂ balls in plastic containers.

As the silica gel is normally white or colorless, and shows no significant change in color during use, it is difficult to tell when gel has become saturated with moisture and needs to be regenerated by heating, or replaced so there is a

need for a visible indication when the gel gets saturated. Traditionally this has been achieved by immersing the gel with a cobalt salt, usually the chloride. This produces a deep blue color for the dry gel, which turns to a light pink as the gel absorbs moisture. Nayak et al. used cobalt chloride as a visible indication of the moisture content of the silica gel for determining whether the gel is saturated or not [38].

Purity of the prepared silica gel depends upon three parameters:

- Water loading by addition of boiled deionized water to silica gel solution before titration with 1 M H₂SO₄ acid.
- Rinse time to remove impurities in silica gel prior to the drying stage
- The reflux time for synthesis of the silica gel.

All parameters have an effect on particle size, surface area and pore size of the resulting silica gel powders [3].

3.2.1 Condition of synthesis

3.2.1.1 Reflux time

Pijarn et al. [3] reported that a key controlling variable for preparation of the silica gel by the sol-gel method is optimum reflux time. The silica gel prepared at a reflux time of 5 h is considered to be optimum since it has smaller particle size and the highest surface area. The SiO₂ gel prepared at a reflux time of 3 h is considered not to be suitable since it has a bigger particle size and lower surface area when compared to 5 h and 9 h reflux time specimens. The silica gel prepared from 9 h reflux may have a pore volume or volume adsorption less than silica gel prepared by 5 h reflux due to the effect of the longer reflux time on its particle size since the 9 h refluxed sample is dense because of

particle agglomeration, and the particle size is small.

3.2.1.2 Rinse time

Rinsing the silica gel twice is insufficient to remove the remnant Na_2SO_4 . Rinsing more than 4 times was found to be necessary to remove the remnant Na_2SO_4 impurity. The particle size is decreased and surface area is increased when the number of rinses increased. The effect of reflux time and rinse time is shown in Figure 6 which shows the TEM of silica gel at various reflux and rinse time.

3.3 Application of silica gel

Due to high surface area ($> 800 \text{ m}^2/\text{g}$) of silica gel, it has a wide range of applications such as a desiccant, as a preservation tool to control humidity, as an adsorbent, as a catalyst and as a catalyst support. Silica gel is a commonly used desiccant as beads packed in a permeable bag. In many items, moisture encourages the growth of mold and spoilage. Condensation may also damage

other items like electronics and may speed the decomposition of chemicals. Through the inclusion of silica gel packets, these items can be preserved longer.

Silica gel may also be used to keep the relative humidity inside a high frequency radio or satellite transmission system waveguide as low as possible. It is commonly known that silica gel is used to dry the industrial compressed air and refrigerants in refrigeration systems. The silica gel absorbs moisture from the compressed air on railway locomotives, where condensation and ice in the brake air pipes can lead to brake failure.

Silica gel is sometimes used as a preservation tool to control relative humidity in museum and library exhibitions and storage. It is also used in packaging of leather products, electronic equipments, metal items, some food products, textiles, pharmaceutical products (vitamin pills) etc. Other applications of silica gel include diagnostic test strips, inhalation devices, syringes, drug test kits and hospital sanitation kits etc.

In chemistry, silica gel is used in chromatography as a stationary phase. In column chromatography, the stationary phase is most often composed of silica gel particles of 40-63 μm . Different particle sizes are used for achieving a desired separation of certain molecular sizes. In this application, due to silica gel's polarity, non-polar components tend to elute before more polar ones, hence the name normal phase chromatography. However, when hydrophobic groups (such as C18 groups) are attached to the silica gel then polar components elute first and the method is referred to as reverse phase chromatography. Silica gel is also applied to alumina, glass, or plastic sheets for thin layer chromatography.

The hydroxyl (OH) groups on the surface of silica can be functionalized to afford specialty silica gels that exhibit unique stationary phase parameters. These so-called functionalized silica gels are also used in organic synthesis and purification as insoluble reagents and scavengers. Chelating groups have also been covalently bound to silica gel. These materials have the ability to remove metal ions selectively from aqueous media. Chelating groups can be covalently bound to polyamines that have been grafted onto a silica gel surface producing a material of greater mechanical integrity. Silica gel is also combined with alkali metals to form an M-SG reducing agent.

Silica gel is also used as cat litter by itself or in combination with more traditional materials, such as clays including bentonite. Silica in this form can

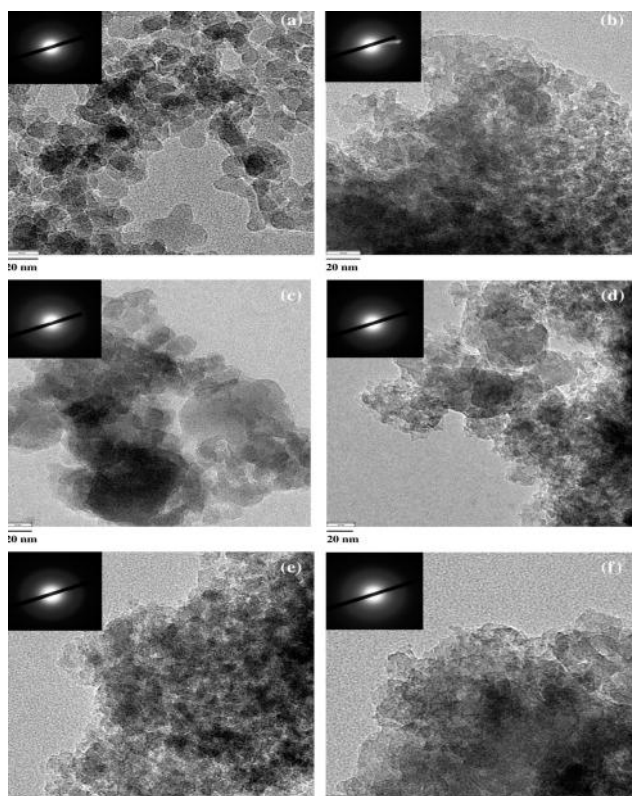


Figure 6. TEM images of SiO_2 gel: (a) fumed silica (b) SiO_2 gel (5 h reflux and 4 rinses), (c) SiO_2 gel (5 h reflux and 6 rinses), (d) SiO_2 gel (5 h reflux and 8 rinses), (e) SiO_2 gel (9 h reflux and 8 rinses), and (f) SiO_2 gel (3 h reflux and 8 rinses) [3].

be a cost effective way for retail consumers easily to purchase silica gel for application in such things as maintaining the desired relative humidity in humidors, keeping tools rust free in damp environments, long term storage, and preservation of dried food for long term storage. Amorphous silica powder is basic raw material used in industries associated with rubber, ceramics, electronics, catalysis, pharmaceuticals, dental material and other materials [15].

4. Silica xero-gel

Silica xero-gel from RHA having 93% silica and 2.6% moisture and is produced by alkaline extraction followed by acid precipitation at pH 7 [24] and at pH 4 with minimal mineral contaminants [38].

4.1. Impurities Present

The major impurities of silica produced from RHA at an extraction yield of 91% were Na, K, and Ca. Acid washing prior to extraction resulted in silica with a lower concentration of Ca (<200 ppm). However, final water washing of the xero-gel was more effective in producing silica with lower overall mineral content (Na < 200 ppm and K < 400 ppm). Acid leaching [42] and gasification [43] methods have been investigated for recovering silica from rice husk. Silica gel produced from RHA using an alkali extraction method had over 65% moisture, 2% of sodium, 0.04% of potassium, 0.01% of calcium and traces (<0.01%) of other elements [37]. Concentrations of Na and K in this gel were relatively high compared to Na and K concentrations in commercial silica. Hence, an effective mineral leaching step is necessary to produce xero-gels with reduced Na and K concentrations from RHA.

4.2. Acid Washing

The initial acid washing did not improve the purity of silica when compared to the purity of silica obtained from unwashed RHA and RHA washed at pH 7. Incorporation of an additional washing step after drying the extracted silica, resulted in a silica product with even lower mineral (Na, and K) content. Washing the dried silica (xero-gel) with deionized water is more effective than washing the silica gel (aqua-gel) prior to drying, in removing minerals from the silica. This could be due to entrapment of metal ions in the silica gel network, which may not be leached out by water washing [24]. Drying silica gel to a very low moisture level might result in disruption of the silica gel network structure and

Table 6. Physical properties of SiO₂ xero-gel [39,40, 41]

Properties	Value	Comments
Thermal conductivity	~0.018 w/k	Determined by Vacuum Insulation Conductivity Tester
Bulk density (ρ)	1.19 g/cm ³	Calculated from refractive index by $\rho = (n - 1)/0.202$
Refractive index	~1.26	Very low for a solid material
Porosity (Π)	47.5%	$\Pi = 1 - \rho/\rho_s$ where ρ_s (thermally grown conventional SiO ₂ film)
Dielectric constant (k)	~2.52	Determined by $k=1+1.28\rho$, (ρ is density)
Surface area	69-152 m ² /g	As determined by nitrogen adsorption/desorption
Pore volume	0.059-0.137 cm ³ /g	Determined by nitrogen adsorption/desorption (varies with density)
Pore diameter	6.4-6.8 nm	Determined by nitrogen adsorption/desorption (varies with density)

would free the trapped mineral ions (Na, and K). Sodium and potassium ions might be easily leached out by washing the dried gel with water. The high sodium content of xero-gel was due to the very rapid gelation at pH 7.0 that effectively trapped sodium chloride in the gel matrix. A mixture of hydrochloric, citric and oxalic acid is used for preparation of silica. The Ca content was comparatively lower for silica prepared from acid washed RHA. This may be due to the fact that, Ca being the major divalent cation in RHA, will require lower pH washing as it is strongly adsorbed on the silica surface at pH>5 [44]. Therefore, to keep the Ca content in silica at a lower concentration, an initial acid washing might be required.

Further, it should be noticed that the silica extraction yields were similar for unwashed RHA, RHA washed at pH 7 and acid washed RHA. Final washing of xero-gel is necessary to keep the overall mineral content at a lower concentration. However, if a very low concentration of Ca is required, acid pre-wash of RHA can be used without any adverse effect on silica yield.

4.3. Production of silica xero-gel

Hong et al. prepared silica xero-gel with a low dielectric constant by a two-step acid-base catalyst

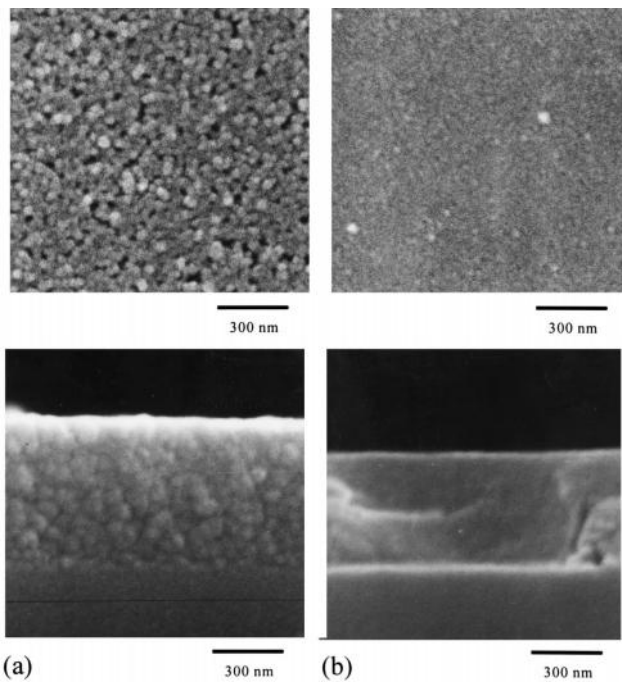


Figure 7. SEM micrographs of SiO₂ xero-gel films; (a) modified and (b) unmodified [41]

procedure and successive surface modification with trimethylchlorosilane (TMCS). Only 15% porosity could be obtained without surface modification but with surface modification the porosity increased to 50%. The surface morphology of modified film is more porous than that of unmodified film. Unmodified film consists of very small size particles (10 nm) and appears to form dense SiO₂ film, but modified film appears to consist of coarse (~40 nm) particles and pores. Modified SiO₂ xero-gel films showed good thickness uniformity, and the average film thickness was measured as 550 nm. This value is larger than that of unmodified film (420 nm) coated under the same conditions [41].

To obtain detailed information on network structure, SiO₂ xero-gel dispersed in ethanol was observed using TEM. The particles shown in Figure 8 have sizes between 30 and 40 nm and build up a 3-dimensional network in SiO₂ xero-gel film.

Kalapathy et al. has prepared silica xero-gel by adding 2 M hydrochloric acid, 1 M citric acid, and 1 M oxalic acid to 50 ml sodium silicate solution prepared from rice husk until the pH 7.0 was obtained and aged for 10–12 h [24]. The silica gels produced were crushed inside the beakers, dispersed in deionized water (100 ml), and centrifuged (1325g) to remove soluble salts. The washing step was repeated two more times and

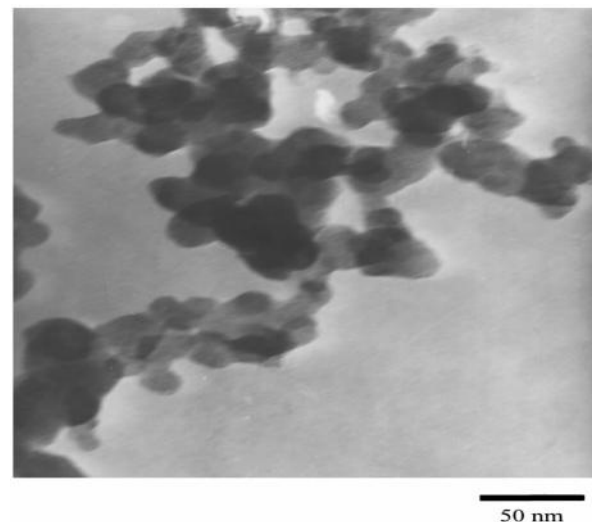


Figure 8. TEM micrograph of modified SiO₂ xero-gel film [41].

then dried at 80 °C for 24 h to obtain pure silica xero-gel [45].

4.4. Effect of pH on production of silica xero-gel

Silica gel could be produced at an acidic pH by adding sodium silicate to an acidic solution. This acidic solution was prepared by adding 6 M hydrochloric acid, 3 M citric acid, 1.5 M oxalic acid to 100 ml deionized water until pH 1.5 was reached then silicate solution was added to acidic solution until pH reached 4. At acidic pH, gelation is slower and hence sodium ions may diffuse out of gel matrix and can be washed out easily to produce high purity silica. It's necessary to add silicate solution to acid solution, instead of adding acid to silicate solution. When acid was added to silicate solution (pH 11.8), silica gel started to form rapidly as soon as pH 10 was reached and formed a rigid gel at pH 7.0. Hence it is difficult to lower the pH below 7.0. At pH 4.0, gel formation was very slow and the gels were comparatively softer (as reflected by lack of firmness) than those produced at pH 7.0.

This is expected, since at pH 7.0, covalent Si–O–Si bonds were responsible for the gel structure whereas at pH 4.0 comparatively weaker van der Waals attraction and H-bonds were the major contributing forces for the gel structure [24]. Hence, at acidic pH the slower rate of gelation provided sufficient time for sodium ion and counter anions to diffuse out of the silica matrix. This diffusion process may have helped to wash out the salts effectively from aqua-gel. Furthermore, at pH 4.0, the silica precipitated using citric and oxalic

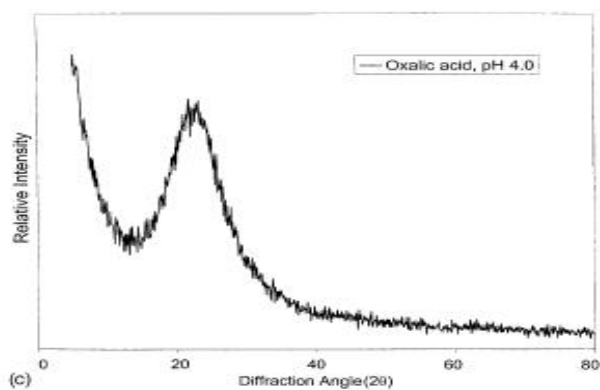


Figure 9. X-ray diffraction pattern of pure RHA silica xero-gel produced at pH 4 using oxalic acid [45]

acid solution had lower sodium content than the silica produced using hydrochloric acid, indicating that water washing was more effective in removing sodium citrate and sodium oxalate from silica gel but not in removing sodium chloride. The XRD spectra of silica produced at pH 4.0 using oxalic acid is shown in Figure 9. A broad peak centered at 2θ angle of 22° confirmed the amorphous nature of the silica [45].

4.5 Silica xero-gel yield at various pH

No significant differences in silica yield were observed with the type of acid used for silica production or the pH of silica precipitation [24]. But Liou et al., reported that silica yield gradually increases with increasing pH, with a maximum yield occurring at around pH 7. When the pH is greater than 8, gels formed are unstable and partially redissolved. At pH 11, these gels dissolve almost completely in water. Experimental results show that optimum conditions for producing silica are gelation at pH 3 with a silicate concentration of 0.15 M with an aging temperature of 50°C and an aging time of 12 h [31]. Surface area of silica strongly depends on pH and decreases as pH increases.

5. Silica Aero-gel

The emerging sol-gel techniques from last few decades have led to a fast progress in the deliberate synthesis of porous material. Out of all known solid porous materials, Silica aero-gels have been widely accepted and used because of their low bulk density, hydrophobicity, low thermal conductivity, high surface area, optical transparency, high porosity, high specific surface area, low refractive index, low sound velocity [46, 47]. They possess a wide variety of exceptional

Table 7. Physical properties of silica aero-gel [48, 49]

Property	Value	Comments
Thermal conductivity	~ 0.01 W/m.K	Determined by Vacuum Insulation Conductivity Tester
Bulk density	~ 0.03 - 0.35 gm/cm ³	Most common density is ~ 0.1 gm/cm ³ and determined by using Helium pycnometry
Porosity	$\sim 99\%$	As determined by BET method
Optical transmission	99%	Determined by Rayleigh scattering theory
Specific surface area	600-1200 m ² /g	As determined by nitrogen adsorption/desorption
Sound velocity	100 m/s	For density = 0.07 gm/cm ³ . One of the lowest velocities for a solid material
% Solids	0.13-15%	Typically 5% (95% free space)
Mean pore diameter	~ 20 nm	Determined by nitrogen adsorption/desorption (varies with density)
Primary particle diameter	2-5 nm	Determined by electron microscopy
Coefficient of thermal expansion	2.0 - 4.0×10^{-6}	Determined using ultrasonic methods
Refractive index	~ 1.05	Very low for a solid material
Dielectric constant	~ 1.0 - 2.0	For density = 0.1 gm/cm ³ . Very low for a solid material

properties as listed in the Table 7.

Many authors have studied the synthesis of silica aero-gels by the use of different precursors and many have focused on modification of synthesis parameters [50,51]. Recently many research works have been devoted to ambient pressure drying which makes the production commercial and industrial [50, 52, 53]. Aero-gels are synthesized from molecular precursor by sol-gel processing. Pore liquid is replaced with air while maintaining the solid network. Special drying techniques are adapted. Supercritical drying is most common however recently adapted techniques involve removal of liquid at atmospheric pressure after chemical modification of inner surface of gels leaving a porous silica network filled with air [48].

5.1 Properties of silica aero-gels and methods of determination

Extensive interest in aero-gels, particularly silica aero-gels, is due to their unusual solid

Table 7. Physical properties of silica aero-gel [48, 49]

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Thermal conductivity	~0.01 W/m.K	Determined by Vacuum Insulation Conductivity Tester
Bulk density	~0.03-0.35 gm/cm ³	Most common density is ~0.1g/cm ³ and determined by using Helium pycnometry
Porosity	~99%	As determined by BET method
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Specific surface area	600-1200 m ² /g	As determined by nitrogen adsorption/desorption
Sound velocity	100 m/s	For density = 0.07 g/cm ³ . One of the lowest velocities for a solid material
% Solids	0.13–15%	Typically 5% (95% free space)
Mean pore diameter	~20 nm	Determined by nitrogen adsorption/desorption (varies with density)
Primary particle diameter	2–5 nm	Determined by electron microscopy
Coefficient of thermal expansion	2.0–4.0 × 10 ⁻⁶	Determined using ultrasonic methods
Refractive index	~1.05	Very low for a solid material
Dielectric constant	~1.0–2.0	For density = 0.1 g/cm ³ . Very low for a solid material

material properties which are described below:

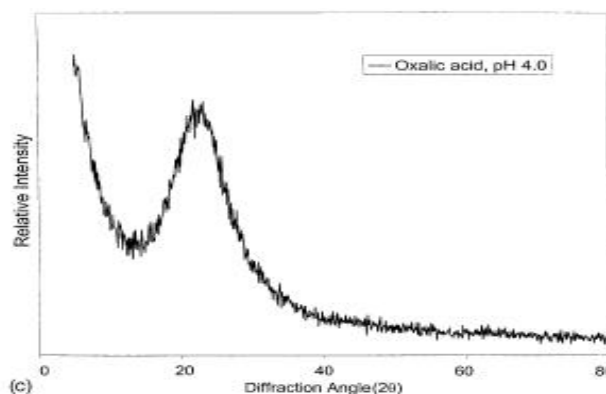
5.1.1 Pore Structure

According to IUPAC classification for porous materials, the pores are classified on the basis of size:

- Micropores: pores having diameters < 2 nm
- Mesopores: pores having diameters between 2 - 50 nm
- Macropores: pores having diameters > 50 nm

Silica aero-gels possess pores of all three sizes [54]. The approximate values of the pore size are between 5 and 100 nm, with an average pore diameter between 20 and 40 nm and a BET surface area between 600 and 1000 m². Porosity can be as high as 99%.

Aero-gel pore network has an “open” nature and interconnectivity. In open-pore structures,


Figure 9. X-ray diffraction pattern of pure RHA silica xero-gel produced at pH 4 using oxalic acid [45]

however, fluid flows from pore to pore, with limited restriction, and travel through the entire material. These pore structures of silica aero-gels, lead to applications as catalyst [55], absorbing media for desiccation [56, 57] and waste containment [58]. Aero-gels have an unusual combination of high porosity and small pore size. The most widely used method for determination of aero-gel porosity is the nitrogen adsorption/desorption technique [59-61]. In this method, the amount of adsorbed gas is measured [62]. Nitrogen-adsorption techniques can, in principle, distinguish various pore shapes by the shape of the isotherms. However, apart from experimental deficiencies [63], the shapes of aero-gel isotherms are very similar. The microstructure of aero-gels can be determined by high resolution scanning electron microscopy (SEM) and transmission electron microscopy (TEM) as shown in the Figure 10 [64].

5.1.2 Density

Volume shrinkage of the aero-gels is calculated from the volumes of the hydro-gel and aero-gel. Two different terms are used to characterize silica aero-gels: bulk density and skeletal density.

- Bulk density (ρ_b) is defined as the ratio of the aero-gel's mass to its volume. This density is obtained by mass and Hg-displacement volume at atmospheric pressure.
- The texture of the solid part of aero-gels is made of ultra fine particles. Skeletal density of these particles is supposed to be very close to that of the solid and it is obtained by using helium pycnometry [65].

5.1.3 Optical Properties

In many procedures, the resulted silica aero-

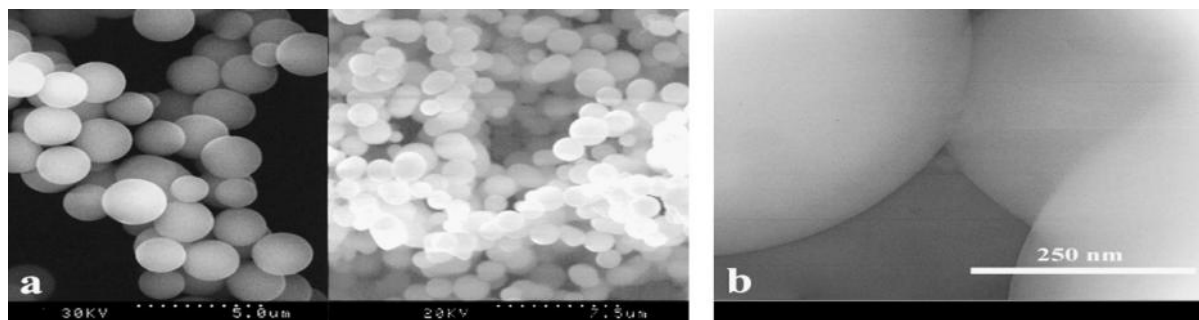


Figure 10. (a) SEM (b) TEM picture, showing the pore characteristics of silica aero-gels [64]

gels are transparent and it is an unusual property for a porous material. This relatively rare combination of traits arises because the aero-gel microstructure has a scale small compared to the wavelength of light. Aero-gels are transparent because there is a small amount of scattering in the visible, the scattered light has a relatively isotropic angular distribution, and exhibits little multiple scattering [66,67]. This behavior can be described by Rayleigh scattering theory. Due to their very high thermal insulation properties and their optical transparency in the visible region, aero-gels were proposed for double plane windows [68, 69]. Heating the aero-gels improves their transparency due to desorption of water and burning of organic components [70]. Also, the optical properties of aero-gels are greatly influenced by the sol-gel process parameters and the type of silation agent [71].

5.1.4 Thermal Conductivity

Silica aero-gels are highly insulating materials having thermal conductivity lower than still air because of their porosity and nanometer pore size. Kistler [19,32] demonstrated that the thermal conductivity of an aero-gel is approximately 0.02 W/mK at ambient pressure in air and in the order of 0.01 W/mK when evacuated [72]. Because silica aero-gels have a very small (~1–10%) fraction of solid silica, thus exhibit a lower solid conductivity and hence, transmit a lower thermal energy. The final mode of thermal transport through silica aero-gels is infrared radiation. The optical thickness of the sample is an important parameter that influences this transfer route and is given as the product of the geometrical thickness and the optical extinction coefficient of the aero-gel. At low temperatures, the radiative component of thermal transport is low, but at higher temperatures, radiative transport becomes a dominant mode of thermal conduction. For measurement of the thermal conductivity, a Vacuum Insulation

Conductivity Tester – VICTOR – may be employed. Some authors reported the use of a hot wire method [73].

5.1.5 Hydrophobicity

Depending on the conditions during synthesis, silica aero-gels can either be hydrophilic or hydrophobic. The main source of hydrophilicity is silanol polar groups Si–OH present in the aero-gel structure, because they can promote the adsorption of water. Generally, aero-gels synthesized by unmodified hydrolysis and condensation of alkylorthosilicates and dried by high temperature supercritical drying (HTSCD) are hydrophobic, and those dried by CO₂ are hydrophilic. This difference is due to the different surface groups formed during the supercritical drying (SCD) process. Low temperature supercritical drying (LTSCD) results in hydroxyl groups (–OH) on the surface resulting hydrophilic aero-gels. HTSCD allows for the reaction of the surface hydroxyl groups with the solvent to form methoxy groups (–OCH₃)X and thus results in hydrophobic aero-gels. Fourier transform infrared spectroscopy (FTIR) is employed to investigate the chemical bonding state of aero-gels [74].

There are two different routes to increase the hydrophobicity of an aero-gel:

- By the addition of a silylating agent during the sol-gel step. This principle is used in ambient pressure drying methods [75].
- By the modification of the aero-gel surface after drying. The surface of hydrophilic aero-gels can be modified by reaction with gaseous methanol [73].

The hydrophobicity of the aero-gels is tested by measuring the contact angle θ , of a water droplet with the aero-gel surface using the formula (1),

$$\theta = 2 \tan^{-1}(2h/w) \quad (1)$$

Where h is the height and w is the width of the

Table 8. Application of silica aero-gel [48,76,77]

Property	Features	Applications
Thermal conductivity	1) Highly Insulating solid 2) Low thermal conductivity 3) Withstand high temperature 4) Transmit lower thermal energy	1) Building construction and appliance insulation 2) Storage media 3) Automobiles, Space vehicles 4) Solar devices, Solar ponds 5) Refrigerator 6) Thermal insulation material for windows
Density/ porosity	1) Lightest synthetic solid 2) High surface area 3) Multiple Compositions 4) Low bulk density	1) Catalysis 2) Sensor 3) Fuel storage 4) Ion exchange 5) Filters for pollutants gaseous 6) Absorbing media for desiccation 7) Waste containment
Optical	1) Transparent 2) Low refractive index	1) Light weight optics 2) Light guides
Acoustic	Low speed of sound	1) Sound proof rooms 2) Acoustic impedance matching in ultrasonic distance sensors
Mechanical	1) Elastic 2) Light weight	1) Energy absorber 2) Hypervelocity particle trap
Electrical	1) Lowest dielectric constant 2) High dielectric strength 3) High surface area	1) Dielectrics for ICs 2) Spacers for vacuum electrodes 3) Capacitors 4) Cherenkov detectors
Chemical	1) Good adsorbent 2) High surface area	1) Adsorbent 2) Catalyst support 3) Extracting agent 4) Nano vessels
Filler	Thickening agent	1) Paints 2) Varnishes 3) Functional liquid

water droplet touching the aero-gel surface. The retention of hydrophobicity is judged from the absorption of water by the aero-gels. Hydrophobic gels exhibit hydrophobicity only for a certain period of time.

5.2. Application of silica aero-gel

Commercial applications of silica aero-gel in thermal window insulation, acoustic barriers, supercapacitors and catalytic supports have been proposed, [76-80]. However, monolithic silica aero-gel has been used extensively in high energy physics in Cherenkov radiation detectors [81-85]. Other application of silica aero-gels are in shock wave studies at high pressures, inertial confinement fusion (ICF) [86], radioluminescent devices [87] and micrometeorites [88]. Silica aero-gels have been widely accepted and used (Table 8) because of their exceptional properties discussed above.

5.3. Synthesis of silica aero-gel

The synthesis of silica aero-gels can be divided into 3 general steps:

a) Gel preparation

The silica gel is obtained by sol-gel process. The sol is prepared by a silica source solution and gelation is occurred by the addition of a catalyst.

b) Aging of the gel

The gel prepared in the first step is aged in its mother solution. This aging process strengthens the gel, so that shrinkage during the drying step is kept to a minimum. Increasing the aging time from 1 to 12 h causes a considerable increase in sample surface area. Further, increasing aging times from 12 to 96 h can cause reduction in surface area [31]. Increasing aging temperature from 20 to 50 °C increases surface area due to accelerated growth of silica framework with increasing aging

temperature. However, when aging temperature increases from 50 to 120 °C, surface area decreases because gelation rate is faster at high formation temperature.

c) Drying of the gel

In this step, the gel should be freed of the pore liquid. To prevent the collapse of the gel structure drying is made to take place under special conditions as described below.

5.3.1 Silica aero-gel production by supercritical carbon dioxide drying

In supercritical drying (SCD) method, the pore liquid is removed above the Critical Temperature (T_c) and Critical Pressure (P_c) of the concerned liquid. At this point there is no liquid–vapour interface and, thus, no capillary pressure [89]. There are two different methods of supercritical drying:

- High temperature supercritical drying (HTSCD)
- Low temperature supercritical drying (LTSCD)

5.3.1.1 High temperature supercritical drying (HTSCD)

HTSCD method is the first method of drying the silica aero-gel. Kistler in 1931 used this method for silica aero-gel production and from then it is being used for the same [72]. Nicolaon and Teichner, [1900–1906, 1968] prepared silica aero-gels by high temperature supercritical drying of a wet gel produced by the hydrolysis of TMOS in methanol [90].

TSCD is done in three steps as follows:

- Silica gel having sufficient amount of solvent (e.g. methanol) is placed in an autoclave and the temperature is raised slowly. Due to this pressure increases. Both the temperature and pressure are adjusted to reach values above the critical points of the corresponding solvent. The conditions are kept constant for a certain period of time when the set temperature and pressure is reached.
- The fluid is then slowly vented at constant temperature, resulting in a pressure drop.
- On attaining the ambient pressure, the vessel is cooled to room temperature. Thus, the phase boundary between liquid and gas is not crossed during the drying process. HTSCD is schematically represented in Figure 11.

Supercritical drying in organic liquids leads to rearrangement reactions in the gel network due to

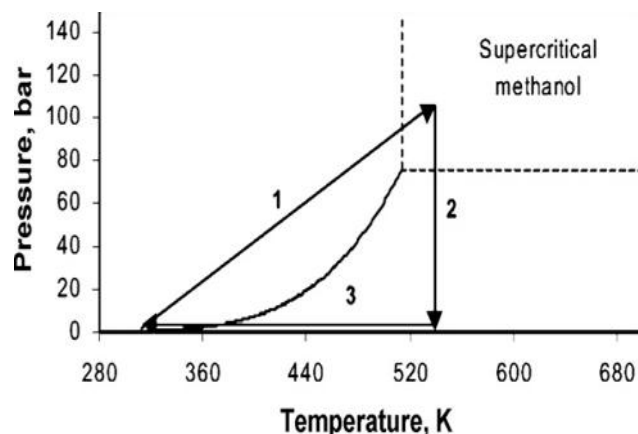


Figure 11. Schematic procedure of high temperature supercritical drying [49]

high temperature conditions. For example, under supercritical conditions, the silica aero-gel surface is reesterified, making the material hydrophobic and stable when exposed to atmospheric moisture.

Poco et al. [91] developed a rapid supercritical extraction (RSCE) for SCD and then further used by [92–94]. In RSCE, rates of condensation reactions were increased due to the increased temperature. Sol was poured directly into a container and heated immediately to supercritical conditions in an autoclave. Gelation and aging occurred during heating and the reaction rates were found to be very high because of high temperatures. Also, the gel filled the container completely, which enabled relatively fast venting of the supercritical fluid. This process seems to be a modification of normal high temperature drying. This method, however, may present problems due to the combination of high temperatures and high pressures as well as the flammability of the solvents.

Many efforts have been carried out for establishing a drying procedure that can be done at moderate temperatures and pressures. Kirkbir et al. observed that a threshold pressure exists above which the shrinkage is negligible. Below the threshold point, the capillary pressure overcomes the strength and the structure collapses. The threshold point depends on sol composition. They managed to reduce the drying pressure (but not the temperature). Several different solvents such as ethanol, butanol, pentanol and isooctane were tested and, in each case, it was found that the drying pressure could be reduced to a certain value, so that shrinkage of the aero-gels did not exceed 5%. They found that shrinkage is negligible

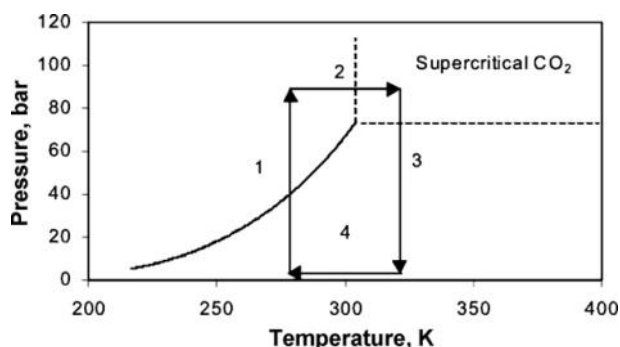


Figure 12. Schematic procedure of low temperature supercritical drying [49]

for wet gels dried in 2-pentanol at 1.8 MPa and 300 °C [95].

5.3.1.2 Low temperature supercritical drying (LTSCD)

Tewari et al. [96] reported an alternative method for drying of silica aero-gel. The solvent present in the gel before drying (generally alcohol) is replaced by a liquid having a critical point close to ambient temperature. The most practical choice is liquid CO₂. LTSCD has the advantage of being implemented at a low temperature (< 40 °C) and moderate pressure (< 80 bar). The whole process is shown schematically in Figure 12.

The experimental procedure has the following steps:

- The gel containing excess amount of solvent (e.g. CH₃OH) is placed in an autoclave. The vessel is sealed and liquid CO₂ is pumped in at 4–10 °C until the pressure reaches about 100 bar. Then the outlet valve is opened so that the solvent extracted by the liquid CO₂, is able to flow out. When CO₂ replaces the solvent completely, the pump is turned off; the temperature is raised to 40 °C (i.e. above the critical temperature of CO₂, T_c = 31 °C) and the pressure is kept constant at 100 bar.
- On reaching 40 °C, and thus ensuring the transition of CO₂ into the supercritical state, the system is slowly depressurized under natural flow.
- When ambient pressure is reached, the system is cooled down to the room temperature. Aero-gels obtained by this method are hydrophilic.

After ten years, a modification in LTSCD process was done such as to involve the use of supercritical CO₂ in place of liquid CO₂. In this process, the heating and cooling steps can be eliminated. The LTSCD process also involves an

extraction step, which strongly depends on the diffusion of CO₂ in the solvent. The LTSCD process has an extraction step, which strongly depends on the diffusion of CO₂ in the solvent. The transport mechanisms of alcohol and CO₂ are described by Knudsen and surface diffusion [95]. The duration of the drying step is difficult to predict, because in most cases the diffusion coefficients of the liquid in the sample are unknown. In order to describe the extraction process, Novak et al. determined binary diffusion coefficients of methanol–liquid CO₂ and methanol–supercritical CO₂.

They found that the diffusion coefficient increases with increasing temperature. But in low-temperature aero-gel production, replacement of an original solvent with liquid or supercritical carbon dioxide is the critical stage and is fully controlled by diffusional mechanism [97]. Wawrzyniak et al. proposed the variation of the effective diffusion coefficient of ethanol in the vicinity of the critical point of CO₂ [98]. But in low-temperature aero-gel production, replacement of an original solvent with liquid or supercritical carbon dioxide is the critical stage and it is one fully controlled by diffusion mechanism. In order to describe the extraction process, binary diffusion coefficients of methanol–liquid CO₂ and methanol–supercritical CO₂ were determined by [97]. They found that the diffusion coefficient increases with increasing temperature.

5.3.2 Comparison of HTSCD and LTSCD

Ehrburger-Dolle et al. performed a comparative study of resulted aero-gels dried by HTSCD and LTSCD methods. They reported that the micro porosity of CO₂-dried aero-gels is significantly larger than that of the corresponding MeOH-dried aero-gels [99]. However, the micro and mesoporous textures of the CO₂-dried aero-gel are equivalent to those of the alco-gel [100]. Dieudonne et al. [101] illustrated by small-angle X-ray scattering (SAXS) experiments, that the aero-gels obtained by CO₂-dried aero-gels have tough solid particles whereas methanol supercritical drying show a smooth surface. However, transparency of the CO₂-dried samples is comparable with that of alcohol-dried samples [96]. Tajiri and Igarashi also studied [102] the transmittance of aero-gels, dried in different supercritical media and gave the same result. It was reported, that for the HTSCD, isopropanol seems to be the most favored medium.

Tang and Wang [17] prepared silica aero-gel from rice husk by the following procedure. First of all, rice husk was burned at 600 °C for 4 hr in

electric furnace to get rice husk ash. A 1.5 g of the ash was mixed with 50 ml 1 mol/L NaOH aqueous solution. The mixture was heated up to its boiling point for 1.5 h with the reflux. After reflux, the mixture was filtered to remove the residues and the filtrate was neutralized using 1 mol/L sulfuric acid to pH = 7 to form silica hydro gel. The ageing of prepared gel was done for 24 hr at room temp. The aged gel was washed using de-ionized water to remove the sodium sulfate resulted from the neutralization. Subsequently, the water in the silica gel was replaced by nonhydrous ethanol. After that, the pretreated silica gel was ready for the supercritical drying.

For supercritical drying, the prepared silica gel sample of about 5 cm³ volume was put into the extraction autoclave, which had a volume of 50 ml. The autoclave was pressurized with CO₂ up to 16 MPa at 25 °C for 24 h. During this period, the ethanol in the silica gel was replaced by liquid CO₂. Then the autoclave was heated to 40 °C with constant pressure at 16 MPa. Dynamic drying was performed with CO₂ flow rate of 1.5 mol/h for 4 h at 40 °C and 16 MPa. Afterwards, the autoclave was slowly depressurized to atmosphere at 40 °C. Finally, dried silica aero-gel was obtained as shown in Figure 13 [17].

Scanning electron micrograph (SEM) of prepared aero-gel (Figure 14) indicates that the aero-gel was a porous material with a continuous meshwork structure. In the SEM photo, the white parts are the bulges in the surface of the aero-gel, while the black parts are pores in the aero-gel [17].

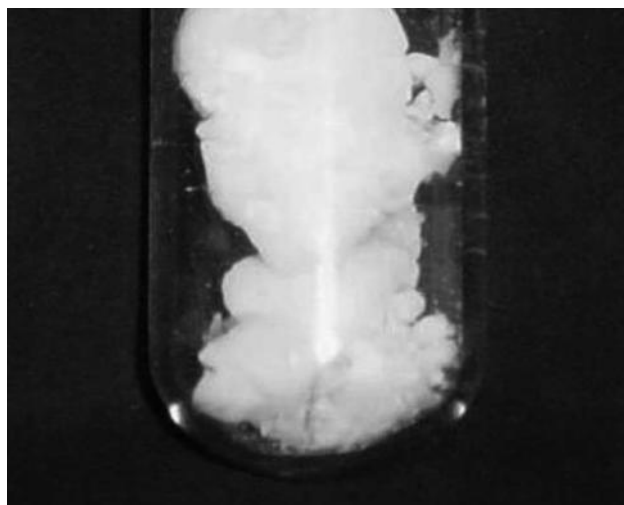


Figure 13. Photograph of prepared Silica aero-gel [17]

5.3.3 Silica aero-gel production by ambient pressure drying

Aero-gels are generally prepared by the supercritical extraction of pore liquid from wet gels, which has certain limitations in terms of its process continuity, cost efficiency because a high temperature and pressure are needed to approach the critical point. The chemical durability of the aero-gels in the atmosphere gradually decreased, if liquid carbon dioxide were used as a solvent in the LTSCD process, since the aero-gel particles are hydrophilic. To overcome these problems, Brinker and Scherer introduced [89] a commercially attractive ambient pressure drying method for the production of silica aero-gel. In this process, the surface of the wet gel is chemically modified by replacing H from hydroxyl groups with hydrophobic functional groups followed by ambient pressure drying. This process creates surfaces with extremely low energies, which dramatically reduces surface tension. Therefore, it is necessary to modify alco-gel surfaces with appropriate modifying agents, so that the surface of the aero-gel is rendered hydrophobic. There are several hydrophobic reagents like methyltrimethoxysilane (MTMS), hexamethyldisilazane (HMDZ), dimethylchloro-silane (DMCS), dimethyldichlorosilane (DMDC), trimethylchlorosilane (TMCS), trimethylethoxysilane (TMES), and hexadecyltrimethoxysilane (HDTMS). Surface modification of the gels through the replacement of H from Si-OH by non-polar alkyl or aryl groups is a crucial step in the ambient pressure drying method. That prevents

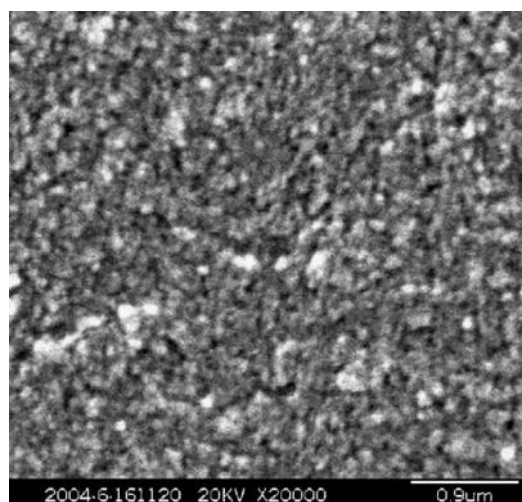


Figure 14. The SEM photo of the silica aero-gel from rice husk ash [17].

condensation reactions of silica clusters, and, by extension, prevents shrinkage of the gel during drying.

For highly porous aero-gel structure, elimination of capillary stress during ambient pressure drying is necessary [103]. Liquid evaporation from wet gel during drying creates a capillary tension (due to the liquid-vapour interface) and that tension is balanced by the compressive stress on the solid network, causing shrinkage of the gel [104]. Strengthening of gel network, surface modification and solvent exchange of the wet gel are necessary to suppress such type of capillary tension and shrinkage during ambient pressure drying [50, 71]. The gel should be aged in silane solution [105] to increase the strength and stiffness of it. Finally, pore liquid must be replaced by low surface tension solvent to reduce capillary stress and associated drying shrinkage.

Nayak and Bera [38] prepared silica aero-gel by ambient pressure drying using the following procedure. They extracted silica from RHA as sodium silicate solution by boiling it in sodium hydroxide solution. Silica was extracted from ash as sodium silicate by boiling it in sodium hydroxide solution. Sodium silicate was neutralized with nitric acid to form silica gel. To prepare aero-gel, first the pore water of the gel was exchanged by ethanol and then surface modification was done by aging alco-gel in tetraethylorthosilicate (TEOS)/ethanol solution. Before drying, TEOS/ethanol solvent was exchanged with n-heptane. Capillary stress and shrinkages were greatly reduced due to the low surface tension of n-heptane. The prepared aero-gel was a light and crack-free solid, with bulk density of 0.67 g.cm^{-3} , porosity of about 80%, total pore volume of $3.1 \text{ cm}^3.\text{g}^{-1}$ and specific surface area of about $273 \text{ m}^2.\text{g}^{-1}$ [38]. Combining the possibilities for gel formation and drying leads to at least two possible routes for ambient pressure dried silica aero-gels:

- Alkoxysilane based aero-gels [106-109]
- Waterglass based aero-gels [50, 51, 104]

Solvent exchange and surface modification are essential to preserve the porous network of the gel before ambient pressure drying (APD). However, solvent exchange is a lengthy and tedious process that involves diffusion of a solution within a gel. The large-scale production of monolithic silica aero-gels at ambient pressure would take several hours or even days because of solvent exchange. Hence, the synthesis of large-scale sodium silicate-based monolithic silica aero-gels at ambient pressure has limitations. In contrast, if silica beads are used, solvent exchange is much faster; this can considerably reduce the production time and cost

[104]. In addition, by synthesizing silica aero-gels beads, improvements in physical and textural properties such as specific surface area, pore size, and pore volume of the resulting aero-gels can be attained compared to monolithic silica aero-gels prepared at ambient pressure. Silica aero-gel beads have recently been synthesized at ambient pressure [110]. Sarawade et al. reported a method to synthesize low-density transparent mesoporous silica aero-gel beads by ambient pressure drying (APD). The beads were prepared by acid-base sol-gel polymerization of sodium silicate in aqueous ammonia solution via the ball dropping method (BDM). To minimize shrinkage during drying, wet silica beads were initially prepared; their surfaces were then modified using trimethylchlorosilane (TMCS) via simultaneous solvent exchange and surface modification [111].

5.3.3.1 Preparation of silica hydro-gel beads using sodium silicate

Sarawade et al. [2010] prepared silica hydro gel beads through hydrolysis and polycondensation of sodium silicate as a silica precursor (molar ratio $\text{SiO}_2:\text{Na}_2\text{O} = 3.02$). To prepare silica sol, aqueous sodium silicate solution was mixed with acetic acid-catalyzed water under continuous stirring. Acetic acid solution was added to the aqueous solution of sodium silicate until the solution pH ~ 4 . This procedure was executed rapidly to avoid sol gelation. Then, the sols were dropped into a container with kerosene as the upper layer and aqueous ammonia solution as the bottom layer. As the droplets come into contact with the aqueous ammonia solution (pH 8), the pH increased to ~ 6 , resulting in polymerization of the silica sol (sol-to-gel formation) and gel bead formation. The silica beads obtained were then immersed in aqueous ammonia solution for 2 h at room temperature ($\sim 25^\circ\text{C}$), and washed with distilled water for 12 h to remove the sodium ions trapped inside the wet beads. After washing, the beads were removed for further simultaneous solvent exchange and surface modification [111].

5.3.3.2 Simultaneous solvent exchange/ surface modification of silica wet beads

For surface modification, wet beads were modified using ethanol/TMCS/n-hexane solution via simultaneous solvent exchange and surface modification. The simultaneous solvent exchange and surface modification process was carried out by immersing the prepared hydro gel beads in ethanol/TMCS/n-hexane solution at room temperature for 12 h. To evaluate the effect of

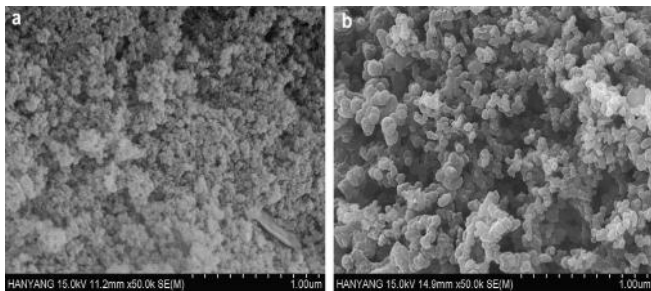


Figure 15. FE-SEM micrograph of (a) unmodified and (b) TMCS modified (10%V of TMCS) mesoporous silica beads [112]

varying percentages of TMCS on the physicochemical properties of the silica beads, the %V of TMCS in the hexane and ethanol solution was varied from 2 to 10%. After surface modification, the beads were washed with n-hexane to remove the unreacted TMCS. The wet beads were dried at room temperature (~25 °C) for 24 h and then at 80 °C for 2 h to reduce shrinkage during drying. To ensure complete evaporation of the pore liquid, the beads were dried at 200 °C for 1 h. It is observed that surface area and cumulative pore volume increases on increasing the volume percent of TMCS.

The mesoporous structure of silica beads was confirmed by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). Fig. 15 shows the pore characteristics and structure morphology of mesoporous silica beads based on FE-SEM micrographs of (a) unmodified and (b) 10%V TMCS modified silica beads. In general, the unmodified

silica beads formed dense aggregates of spheres while the modified silica beads had highly porous structures Figure 15 (b). This is because the unmodified wet gel silica beads shrank more during APD, resulting in dense aggregates of dried silica beads and the loss of mesopores [111].

5.3.4 Silica aero-gel production by Freeze Drying

Phase boundaries between the liquid and the gas phase during drying can also be avoided by freeze drying. In freeze drying, the pore liquid is frozen and then sublimed in vacuum [113-115]. However, the aging period must be extended to stabilize the gel network, the solvent must be replaced by one with a low expansion coefficient and a high sublimation pressure, and salts are added for attaining low freezing temperatures. Another disadvantage is that the network may be destroyed by crystallization of the solvent in the pores. Cryogels are therefore only obtained as powders [48]. Comparison between silica aero-gels prepared with different precursors and drying methods is tabulated below (Table 9).

6. Comparison of Silica Aero-gel and Silica Xero-gel Characteristics

Figure 16 shows comparison of the networks of wet sol-gel, xero-gel and aero-gel. Silica xero-gel is normally synthesized by sol-gel process and is formed once the gel is dried under ambient condition [117].

The morphology of silica matrices was investigated and FE-SEM micrographs are

Table 9. Comparison between silica aero-gels prepared with different precursors and drying methods

Precursor/ drying method	Surface Area (m ² /g)	Modifying agent	Pore Volume (cm ³ /gm)	Color	Pore diameter (nm.)	Bulk density (kg/m ³)	Refer- ence
RHA/ Sc-CO ₂ drying	597.7	-	8.65	White	10	38	[17]
RHA/ Ambient pres- sure drying	917	TMCS	2.3	Semi- transparent	12.3	81	[111]
RHA/ Ambient pres- sure drying	273	TEOS	3.1	Semi- transparent	-	67	[38]
TEOS/ Sc-ethanol drying	935-1150	-	8.6-10.9	transparent	-	43-89	[116]

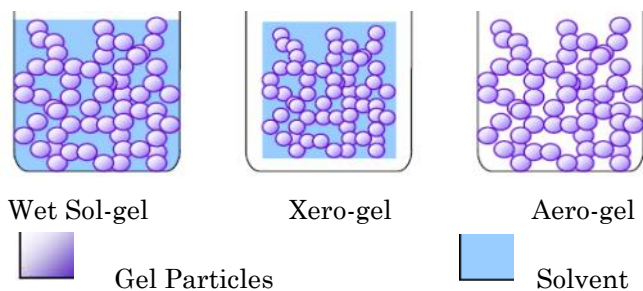


Figure 16. Comparison of gel network of wet sol-gel, xero-gel and aero-gel [117].

illustrated in the Figures 17 and 18. The synthesized silica aero-gel exhibits porous network structure, which contains solid clusters of 10-60 nm and pores below 100 nm in between them (Figure 17). As can be seen in Figure 18, silica xero-gel has a highly dense morphology, which appears as tiny spherical nanoparticles, approximately 30-60 nm in diameter. The micrograph also shows the aggregates of particles in silica xero-gel. Besides that, the diffractograms reveal that the silica aero-gel and silica xero-gel are amorphous (Figure 19). Surface area of silica aero-gel is about three times higher than silica xero-gel. Silica xero-gel possesses lower surface area than silica aero-gel.

7. Conclusion

Rice husk, an agro waste, if burnt under controlled conditions, can be a source for many silicon-based materials. White amorphous silica of high chemical purity, X-ray amorphous, ultra fine in size and having high surface area and reactivity can be produced by acid treatment of rice husk followed by controlled burning. Applications of the rice husk silica are as filler in polymeric materials, as a possible substitute for condensed silica fume in high strength concrete, starting material for high performance silicon compounds etc. Silica aero-gels are used in variety of technological areas because of its extraordinary properties. Substantial progress has been made in the development, processing and characterization of aero-gel materials over the recent years. Special attention has been paid to the use of inexpensive precursors such as rice husk and the drying technology to make the production commercial. The unique optical, mechanical, acoustic, and thermal properties of aero-gels originate from the combination of a solid network and nanosized pores filled with air. The choice of the precursors and the optimization of sol-gel parameters

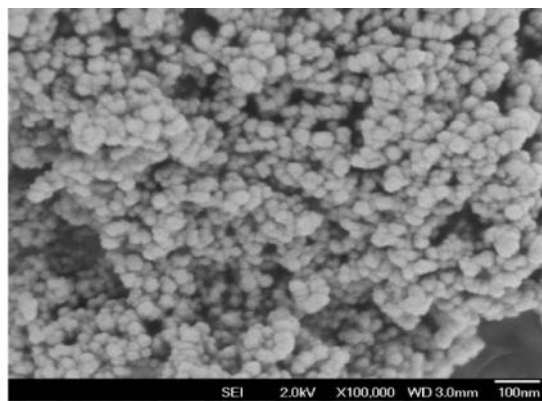


Figure 17. FE-SEM micrograph of synthesized silica aero-gel [117]

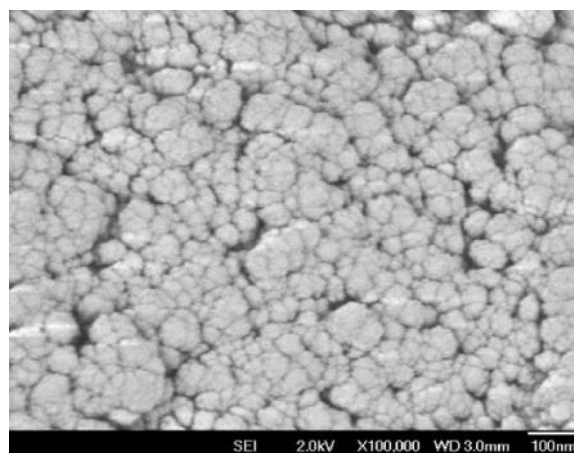


Figure 18. FE-SEM micrograph of synthesized silica xero-gel [117]

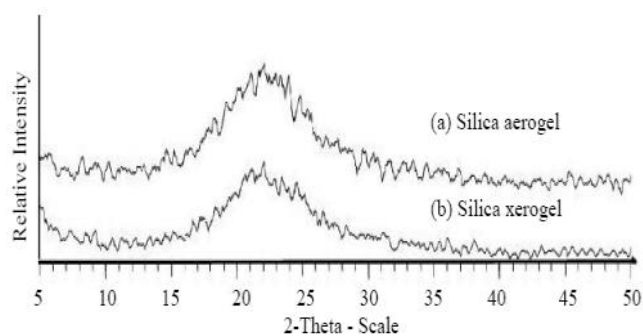


Figure 19. X-ray diffractograms of (a) silica aero-gel, and (b) silica xero-gel [117]

determine the physical properties of the final aero-gel product. Drying of the alco-gels is carried out with supercritical or ambient pressure drying methods, depending upon the commercial aero-gel application. An extensive chemical modification provides a new space for studying the property of

aero-gels. Ambient pressure drying techniques will probably make industrial preparation much cheaper and will thus make aero-gels more competitive. The most important area for the application of aero-gels is in all kinds of thermal insulation, nontoxic, nonflammable, easy to dispose of compared with most of other materials in the market. Economy of the manufacturing process improves if the fuel value of the material is also utilized. Tremendous scope exists for further research and development activities to convert all the laboratory findings into commercial production with appropriate technologies.

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