

EFFECT OF OXALIC ACID AS A CATALYST AND DRY CONTROL CHEMICAL ADDITIVE (DCCA) FOR HYDROPHILIC AEROGEL BASE SODIUM SILICATE BY AMBIENT PRESSURE DRYING

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Ultra-light porous hydrophilic silica were prepared by sol gel neutralization chemical method under the ambient temperature under the effect different molar ratio of oxalic acid (1, 2, and 3), to study its effect on the structure of silica aerogel based on water glass ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) used as the precursors. The gel was washed with deionized distilled water four times for 24 hours. The pH of the gel has a constant value of about 8. Time gelation occurs during (10-25) minutes depending on the acidic molar ratio. The diagnostic analysis is taken by Fourier transition infrared (FTIR), field emission scanning electron microscope (FESEM), and X-ray diffraction (XRD). The material products have a lightweight with low density ($0.35 - 0.27 \text{ gm/cm}^3$). It was floating in the water by its low weight despite its hydrophilic characteristic property. All the diagnostic results matching conformity to most published research results which will also be explained in the present study.

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1. Introduction

Silica Aerogel was discovered by Kistler in 1931 [1, 2]. Aero-silica is an advanced and new material in the field of materials science. It has a weak structure of silicon dioxide that makes up 4%, and the remaining 96% is filled with air, and thus it is considered one of the lightest solid materials ever [3, 4].

Aerogel silica materials have become very popular possessing many properties like optical transmission (99%), high porosity (99%), and low thermal conductivity ($\sim 0.01 \text{ W / mK}$). Furthermore, dielectric constant (1.0--2.0), the specificity surface area ($1000 \text{ m}^2/\text{g}$), speed sound (100 m / s) and low refractive index (1.05) and [5, 6].

Sodium silicate (water glass) or aqueous sodium silicate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$) is an inorganic compound known, easily soluble in water, which has (12.5) pH number 12.5 [3]. Commercially, the water glass is made by reacting NaOH or NaCO_3 with quartz in high pressure and heat environment. These materials are cheap and available in nature, water glass, consider the least expensive industrial materials to give the molecule (selenium – oxygen, and sodium with two ion), it's dissolved in the water and prevents the spontaneous production of the silica at the large amount due to electrostatic forces. Also, it hasn't flammability risk and easy to handle such as silicone alkoxides which included Tetramethylorthosilicate and Tetraethylorthosilicate. Chemically stable for a long time under normal conditions. This type of reactant possesses is the most major advantages of preparing aerogels on an industrial scale [6, 7, 8].

To prepare silica aerogels by chemical technique, it is very important to determine the sol-gel structure and physicochemical [6]. This process generally starts with the mixing of precursors (e.g. Tetraethylorthosilicate (TEOS), Tetramethylorthosilicate (TMOS), and sodium silicate (Na_2SiO_3)) in water mixed with a suitable solvent (usual alcohol) at ambient or slightly elevated temperatures. This mixture is a liquid at the creation of the reaction sol. Sol is a colloidal character with dispersing of the solid or large molecules at (1-1000 nm) in the dimensions [7, 8].

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Quite a lot of research and studies on various factors affect the silica gel production like the molar ratio of precursors and water [8], temperatures [9], hydrolysis amid due to acid and base catalyst [9, 10]

The fluidity of the reactants ends upon completion of the reaction, the formation of the entire reaction mixture is known as the aerogel, which is transformed by the original "sol-gel process" with the removal of the liquid from the wet gel without significant shrinkage and the collapse of the pores. This complete exchange of pore fluid depends on the degree of diffusion solvents and reagents transform into a gel [11]. Fig. 1 illustrates the transition sol to gel under the oxalic acid effect.

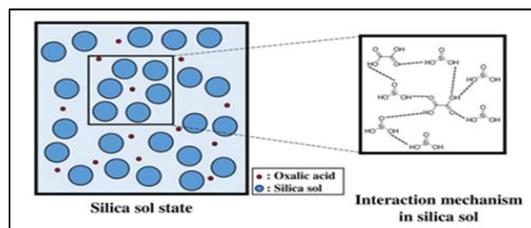


Fig. 1. Sol is transformed into a gel by the action of oxalic acid [14].

To improve the hardness of the resulting gel and increase the size and uniformity of pores, chemical additives for drying control (DCCA) have been used, such as formamide (NH_2CHO), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), dimethylformide (DMA), and acetonitrile [12]. Besides, the hydrolysis of formalid enhances the roughness of the gel [12, 13, and 14].

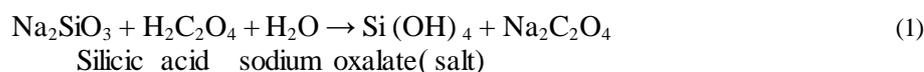
Synthesis of the silica gels from silicon-containing precursors. The simple neutralization induces the production of the gelation of water glass directly [3]. The resulted silica gel characteristics depended on the acid type, solvent type, silicon-containing precursor type, drying, pH, aging, and ion level [14].

In our work we use the first method to preparation of the hydrophilic pours silicate ultra-light, and the current study showed the physical characteristics and the structural changes depended on the molar level of oxalic acid. Figure 1 illustrates the transition sol to gel under the oxalic acid effect.

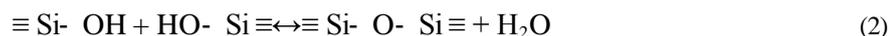
2. Experimental procedure

A simple experimental procedure was used to prepare the hydrophilic silica aerogels at ambient temperature using the Na-silicate solution as a precursor. The chemicals used were a sodium silicate solution ($(\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O})$ sodium metasilicate pentahydrate, (LR THOMAS BAKR India,) as a precursor. Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) AAG panreac Barcelona Espana is used as a catalyst for the gelation and activator chemical to control the solution drying (DCCA). Double-distilled water was used to prepare sodium silicate. Ethanol AR 100% ($\text{C}_2\text{H}_5\text{OH}$ Alpha chemika, India and n-Hexan, 96%, analytical grade, ASC Scharlau chemical Company both used as solvent exchange.

The first step to getting silica aerogel based was sodium silicate solution prepared by stirring for 10 min to get homogenous hydrolysis, it kept for four hours to complete the hydrolysis.



A salt (sodium oxalate) is created, which must be removed by washing with distilled water or by used an ion-exchange column [7], Hydrolyzed Silicate links together forming siloxane bridges [14].



The solution was mixed and stirred to get a mixture of a homogenous solution whose main component is sodium silicate, by adding the catalyst 1, 2, and 3 M of the oxalic acid solution, which played the two important roles as a basic component, the first one as activator chemical to control the solution drying, and the second is the catalyzed by a wise drop to the sodium silicate solution to reach 8 pH values and it is important to get a product formation of silicic acid from sodium silicate, hydrolysis and sodium oxalate gradients $\text{Na}_2\text{C}_2\text{O}_4$ as salt.

While maintaining the pH between (12.5-8), it's clear that the various volumes for the prepared gel obtained with different molar concentrations as shown in figure (2). In acidic media, SiO_2 acts with water to form the hydrated forms of silica that produce the silica gel.

In the case of high pH values ($\text{PH}>7$) the silanol groups will all be negatively charged in silicon dioxide particles as well as the monomers. This speeds up the growth of the particles by adding the monomer resulting in the formation of a silica precipitate, So, In the case of lower pH ($\text{PH}<7$), the addition of particles and the aggregation process results in the formation of a gel instead of a precipitate [14]. A pH affects the state in which accumulation of the particles together and forms the charge, and then the condensation reaction increases with increasing acid concentration so that this affects the crystallization time and the physical properties of the gel such as increasing the viscosity [4].

After the gel-forming, it kept at (50) ° C in an oven for three hours. It aids the Si-OH condensation reaction on the surface of the gel and converts it to a thick layer. Thus, it's become broadly high mechanical strength of the wet gel [12]. After that, the gel is cut to give small granules then four times washed with distilled water to remove the sodium ions from them and purify the silica so it has been soaked for 24 hours such as shown in Figure 2 (A), and Fig 2 (B) illustrates gel transparency degrees with acid concentration. Sample 1M has the highest degree of transparency.

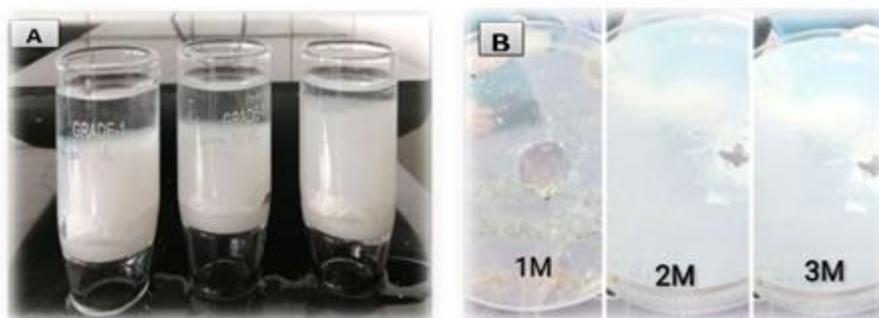


Fig. 2. The prepared samples stages; (A) gel preparation under the washing step, (B) gel transparency degrees with acid concentration.

The wash water is replaced with the solvent ethanol at 50 ° C soaked for 24 hours. Then it is replaced with another solvent with less capillary property [8], which is Hexane, and it is also soaked with it for 24 hours. The reactants are sealed and kept in an oven (50) ° C for one day to improve the network strengthen. The gels were dried by oven (50) ° C for 72 hours, after which the temperature was gradually raised to 200 ° C for 2 hours. Fig. 3 gives a schematic diagram of the stages of the experimental process.

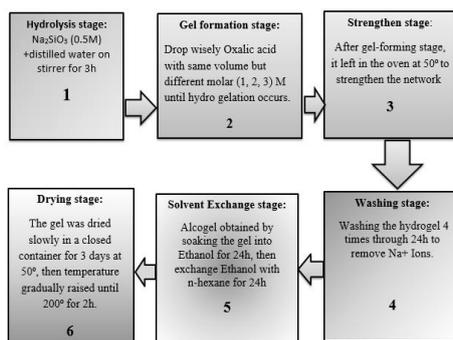


Fig. 3. Chart illustrates the stages preparation of silica aerogel.

Measurement of the density was done by ratio of the mass to volume ratio. A specific volume of the aerogel powders filled with a cylindrical column to get a specific volume of aerogel, whereas electronic microbalance three accuracy digits are used to calculate the mass [12]. The gel was so light so it floats in water as shown in Fig. 4.



Fig. 4. The last shape of the silica aerogel prepared and the floating property.

From the Fig. 4, it becomes clear that sample 3M has the largest volume, higher mass, higher density, more cohesion, and less cracking compared to sample 1M has more fragile cracking and less production and density.

The percentage of shrinkage ($V\%$) calculated from the change in the volumes of the alcogel and the aerogel using the following formula 1 [18] :

$$V\% = \left(1 - \frac{V_1}{V_2}\right) \times 100\% \quad (1)$$

V_1 and V_2 is the volume of the aerogel and alcogel respectively.

Table 1. The physical properties of the silica ultralight.

/	Oxalic acid molarity	Gelation time t_g (min)	Gel appearance	Density g/cm^3	Shrinkage %
A1	1M	20	Transparency	0.23	80
A2	2M	12	Semi-transparency	0.27	76
A3	3M	8	Opaque	0.35	68

3. Structural analysis

3.1. Fourier transmission analysis (FTIR)

Generally, FTIR is known for Silica gel $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ has energy bonds known in most scientific sources (800 is weak, 948 is weak, 1090 is very sharp, 1190 is very small, 1640 is very weak) [1-19]. The information of this research results was confirmed that the resulting material about the different chemical bonds responsible for the hydrophilic properties, such as O-H, Si-OH, and Si-O-Si using spectroscopy. Since the backbone of silica aerogel has consisted of Silica in all bands in the three samples the effect of increasing oxalic acid concentration appeared to increase the width of the IR beam broader and decrease in intensity. Due to the increased crosslinking of the polymerization, which causes scattering of the reflected IR beams? The concentration of one (1M) was recorded at the highest transition intensity and the sharp bands.

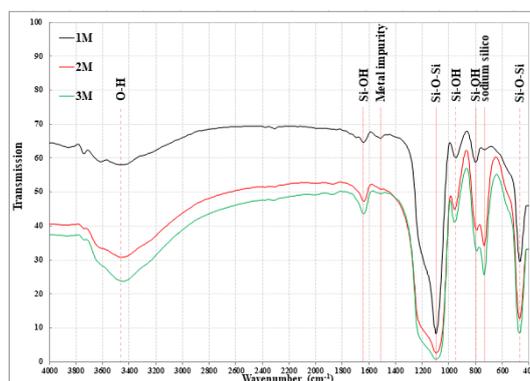


Fig. 5. FTIR analysis for samples of silica aerogel with a different molar oxalic acid catalyst.

The first peak located at 467.75 cm^{-1} in the sample (1M) returned to the symmetric, asymmetric, and deformation vibration for Si-O-Si bonds are presented in all spectra of the three samples not affected with the molar acid change and still the same location to 469.75 cm^{-1} , 470.7 with sample 2,3 respectively. Peaks wave numbers at $(735.31, 735.1 \text{ cm}^{-1})$ appear just with samples 2M, 3M which indicated the presence of the element sodium associated with silica, sodium silico, or indicating sodium oxalate as a salt product due to the original precursors is sodium silicate has high content from Sodium 33% appear clearly with a high concentration of acid catalyst.

Table 2. Locations and origin all bands measured.

Band Type	Wave number (cm^{-1})		
	1M	2M	3M
O-H	3462.00	3455.32	3442.55
Si-OH	1641.00	1638.30	1638.30
Metal impurity	1514.34	1506.68	1506.38
Si-O-Si	1098.27	1094.62	1094.62
Si-OH	949.76	957.40	957.20
Si-O-Si	800.99	794.90	792.87
Sodium indication	735.31	735.1
Si-O-Si	467.7	469.75	470.7

Table 3. The parameter for experimental x-ray results of sample 1M.

2 θ (Deg.)	FWHM (Deg.)	d _{hkl} Exp.(Å)	Crystallite size (nm)	Phase	hkl
20.0180	0.2255	4.4320	35.8	SiO ₂	(311)
21.1004	0.3157	4.2071	25.6	SiO ₂	(004)
26.7829	0.2255	3.3260	36.2	Na ₆ Si ₈ O ₁₉	(151)
27.3241	0.2255	3.2613	36.3	SiO ₂	(213)
29.2183	0.3608	3.0540	22.8	Na ₆ Si ₈ O ₁₉	(015)
31.6536	0.1804	2.8244	45.8	NaCO ₂	(111)
39.4558	0.2706	2.2820	31.2	Na ₆ Si ₈ O ₁₉	(222)
45.4540	0.2706	1.9938	31.8	SiO ₂	(720)
50.7757	0.2706	1.7966	32.5	Na ₆ Si ₈ O ₁₉	(186)
55.2405	0.2255	1.6615	39.8	Na ₆ Si ₈ O ₁₉	(275)
56.0600	0.2705	1.6392	33.3	Na ₆ Si ₈ O ₁₉	(0116)
57.9916	0.2706	1.5891	33.6	Na ₆ Si ₈ O ₁₉	(168)
66.1545	0.2706	1.4114	35.0	NaCO ₂	(214)
75.2646	0.2706	1.2616	37.1	NaCO ₂	(018)

3.3. Field Emission Scanning Electron Measurement (FESEM)

FESEM Tescan-mira III Czech Republic was used to determine the microstructure of silica aerogel based on sodium silicate, Exhibits spherical silica particles. Sample 3M has macro pores (1245nm) big in size, smaller in number thickness agglomeration wall(145nm) due to The particle aggregation was more due to the acceleration of the higher condensation reaction generate opaque gel although larger air cavities in size produced a larger mass with less shrinkage volume (V% <<) and higher density than samples 1M and 2M. The aerogel materials, which possess abundant interconnected macropores or mesoporous, have drawn great interest for their unique properties, including low density; porosity arises from the assumed packing of primary particles in the agglomerates.

Fig. 7 shows the FESEM images of the aerogel samples prepared, it's clear a well-defined and interconnected 3D porous network, in the range of (230nm-1245nm). The effect of molarity cause increasing in pore size.

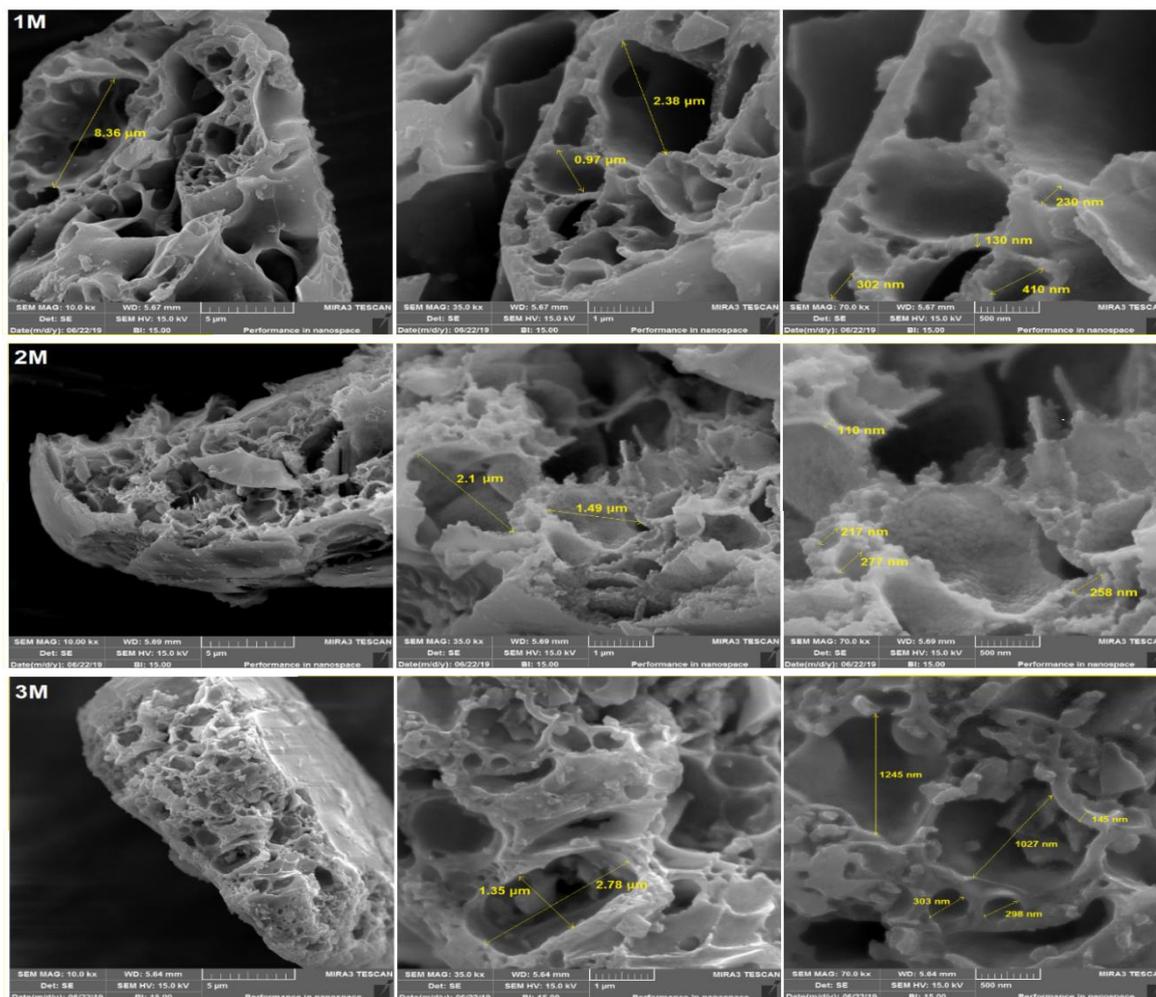


Fig. 7. shows the FESEM images of the aerogel samples prepared with different oxalic acid molar ratio.

4. Conclusions

Crystalline silica aerogel has been successfully prepared using economic raw material (Na_2SiO_3) as a precursor under the ambient temperature. The XRD revealed the silica has the same properties crystalline phase at size (34) nm. The FTIR indicates the silica present in the form of Si-O-Si, the concentration of one (1M) was recorded at the highest transition and the sharp bands.

This silica aerogel showed interconnected macropores or mesoporous shaped morphology as confirmed using field emission scanning electron microscope analysis, which has drawn great interest for their unique properties, including low density in the range ($0.35 - 0.27$) gm/cm^3 . Hydrophilic characteristic property for the prepared aerogel samples were floating in the water by its low weight.

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