Investigation of the preparation pH value influence on the single step silica Aerogel monolith porosity

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Abstract: The influence of acidic and basic environment of sol on the final Aerogel properties was studied in this work. Transparency of silica Aerogel monolith was investigated according to their initial preparation pH values. The findings show that silica Aerogels' optical transmittance is highly sensitive to the pH values employed in their production. Specifically, the silica Aerogels prepared at a pH of 8 demonstrate the highest level of transmittance. SEM as well as BET measurements of silica Aerogels are employed as pore structure probes to ascertain the changes, that occur in a TEOS precursor silica gel, as a function of the variation of the initial preparation pH value. There is a systematic correlation between sol acidic/ basic environment variation and Aerogel surface area except around pH 2 which exhibits abnormal results. While the relation between porosity as well as pore size and preparation pH values were more irregular.

***Keyword*:** aerogel, Sol-gel, pH, surface area, pore volume.

1. Introduction.

Aerogels have been acknowledged for over eight decades, with the initial production of aerogels credited to S. S. Kistler in 1931 [1]. Aerogels can be synthesized by the sol-gel technique, which involves the supercritical drying of the wet gel in an autoclave. Sol-gel processing offers several potential advantages, such as the attainment of materials with high levels of purity, homogeneity, and controlled porosity.

Aerogels possess a porous structure characterized by an extensive interior surface area. Aerogels possess a multitude of remarkable qualities, including but not limited to their exceptionally low density, large specific surface area, and high porosity [2,3]. Thus, these materials show promise in many different areas [4,5], such as catalysis, fuel storage tanks, low dielectric constant materials, and fine particle collection.

Environmental pH affects the kinetics of reactions like polymerization and monomer addition. Husing and Schubert provide a significant overview of Aerogels in their introductory work [6].

1.1. Catalysis mechanism during the sol gel process

Iler (1979) categorizes the process of silica polymerization into three distinct pH domains: pH values below 2, pH values ranging from 2 to 7, and pH values above 7 [7]. The solubility of silica is significantly limited when the pH is below 2. Consequently, primary silica particles tend to form and aggregate, with ripening playing a minor role in their expansion after the particles exceed a diameter of 2nm. Therefore, the coordination of forming gel networks occurs at the level of highly minute primary particles [8].

There is a consensus among scholars that within the pH range of 2 to 6, condensation reactions exhibit a preference for the formation of bonds between species that are more strongly condensed and those that are less highly condensed and possess a degree of neutrality. The presence of chain ends and the drastic decrease in monomers both contribute to the crystallization process. The development of silica particles ceases within this pH range after their diameter reaches around 2-4 nm [9]. When the pH exceeds 7, the condensed species undergo ionization, resulting in mutual repulsion. Instead of particle aggregation being the primary growth driver, the integration of monomers into the more densely packed particles is [10]. Nevertheless, it can be generally asserted that silicon oxide networks formed from the Sol-Gel process, when subjected to acid-catalysed conditions, predominantly produce linear or randomly branched polymers. In situations where a base is used as a catalyst, the resulting clusters exhibit a higher degree of branching and do not interpenetrate before the gelation process. As a result, these clusters behave as separate and distinct entities [8].

Gas adsorption is a commonly employed technique for the characterisation of porous substances, as indicated by its widespread usage [11]. The amount of gas needed to form a monolayer on a solid surface can be measured according to the isothermal adsorption theory developed by Brunauer Emmett Teller (BET). Therefore, this method can be used to analyse Aerogels' specific surface area and pore size distribution. The measurement of gas adsorption typically involves the representation of the amount of gas adsorbed in terms of its volume at standard conditions. The graphical representation of the amount of gas adsorbed as a function of relative pressure is frequently depicted as adsorption-desorption hysteresis loops.

The classification of the bulk of these hysteresis loops is determined by the International Union of Pure and Applied Chemistry (IUPAC), as depicted in Figure 1 [11].

The image provides a concise description of the various pore structures seen in the system. H1 represents well-defined cylindrical pore channels, H2 corresponds to disordered pores characterized by pore blockage and percolation events, H3 depicts non-rigid aggregates of plate-like particles resulting in slit-shaped pores, and H4 denotes narrow slit pores, including those found in the micropore region. The utilization of this conventional representation was employed in the present study for the purpose of analysing the BET measurements.

Additional physical characterizations of Aerogels have been utilized to investigate the impact of pretreatment pH values.

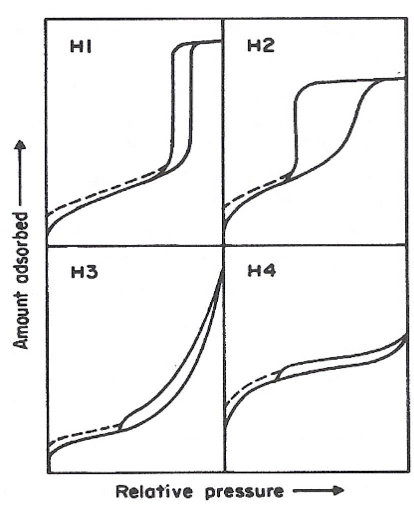

Fig. (1): Types of hysteresis loops.

2. Experimental

2.1. Materials

Tetraethylorthosilicate (TEOS) with a purity of more than 99.0% was purchased from Sigma Aldrich in Germany and used in the synthesis. Sigma Aldrich in the United States supplied the spectroscopic grade ethyl alcohol (C2H5OH) with a purity of 200 proof and greater than 99.5%. We ordered N,N-dimethylformamide (C3H7NO) from the German company Sigma Aldrich with a purity of greater than 99.0%. Amresco in the USA provided deionized water that was HCl-catalysed at a concentration of 0.15 M and a purity greater than 99.0%. Sigma Aldrich in Germany supplied deionized water with a purity greater than 98.0% by ammonium fluoride catalysis. Finally, BDH(Philips) in the USA supplied the deionized water that was catalysed by ammonium hydroxide (H5 NO) at a concentration of 28-30%.

2.2. Procedure

Silica gels were synthesized using a one-step technique. The components used in the synthesis included tetraethylorthosilicate (TEOS), ethanol, water, and either hydrochloric acid or NH4OH. The volume ratios of these components were maintained at 2.5:10:2:X, where X was changed to obtain a final sol with a pH ranging from 1 to 10. The samples were subjected to magnetic stirring at a temperature of 303 K for a duration of 15 minutes. Subsequently, a volume of 0.5 ml of C3H7NO was introduced as a drying control chemical additive (DCCA) and allowed to react for an additional duration of 1 hour while being subjected to magnetic stirring. The sol obtained was permitted to undergo gelation within plastic tubes with a diameter of 1.35 cm. Subsequently, the sol was aged within these tubes for a duration of 22 hours at ambient temperature. To eliminate any residual monomer inside the gel matrix, a series of five 24-hour washes were conducted using pure ethanol. Each wash stage involved the utilization of fresh ethanol.

2.3. Characterization of Aerogels

In this study, the transmittance of the Aerogel samples was measured using a UV-VIS spectrophotometer (Ultrospec 4300 pro). The calibration of sample transmittance was conducted based on the thickness of Aerogel samples, taking into account their inherent brittleness and imperfect forms. Each curve's average transmittance was calculated by numerically integrating the area under the transmittance curve for wavelengths between 400 and 700 nanometers (nm). Aerogels' apparent density was calculated using the formula =m/V, with the use of precise weight measurements of known-size samples. The scanning electron microscopy (SEM, ULTRA 60) technique was employed to examine the morphology and microstructure of the silica Aerogel samples.

Using the micromeritics ASAP 2020 equipment, the pore size distribution and specific surface area of the Aerogel samples were calculated using the Brunauer-Emmitt-Teller (BET) method.

Subsequently, the desiccated Aerogels underwent a heating process, reaching a temperature of 700 °C, with a heating rate of 60 °C per hour.

3. Results

3.1. UV-VIS test

Figure 2 illustrates the relationship between the transmittance of Aerogel samples and the wavelength, with consideration given to the final preparation pH values ranging from 1 to 10.

It is noteworthy that samples with pH values of 5, 6, 7, and 10 demonstrate the lowest levels of transmittance across the whole visible (VIS) region. Conversely, samples with pH values of 1, 3, 8, and 8 exhibit higher levels of transmittance. Meanwhile, samples with pH values of 2 and 4 display intermediate levels of transmittance.

Figure 3 illustrates the transparency values of silica aerogels at various initial preparation pH levels.The results indicate that the silica aerogels with a pH of 8 exhibit the highest level of transmission.

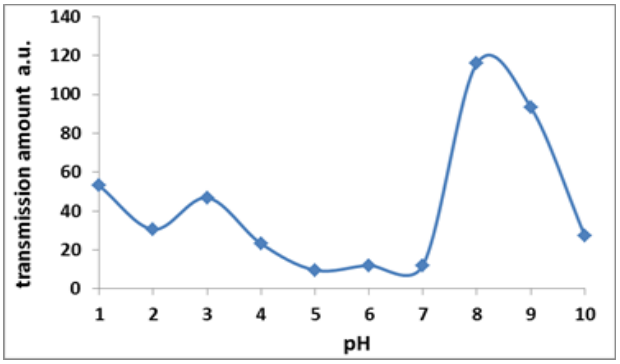

Fig. (2): Transmittance spectra of Aerogel samples at several pH values
(a acidic ,b base).

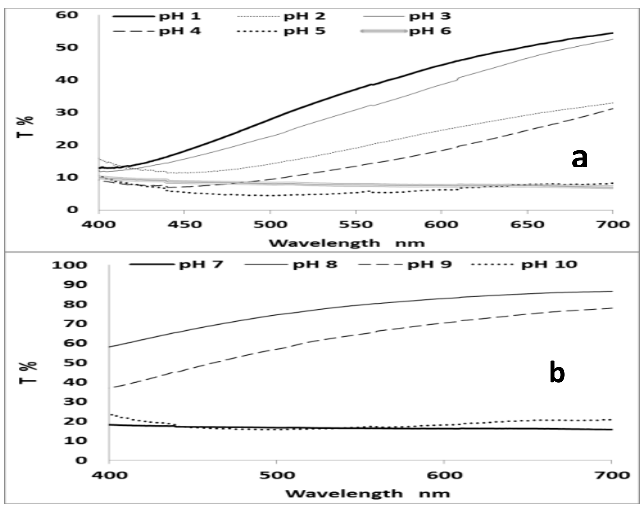

Fig. (3): Effect of the final preparation pH value on the silica Aerogel transmittance.

3.2. Surface area and pore size measurements.

The catalyst systems underwent characterization using BET Nitrogen adsorption-desorption. The pore volumes and surface areas of the silica Aerogels were determined through the utilization of nitrogen sorption measurement. The BET analysis method was employed to determine the pore volume using a single condensation point at $P/Po = 0.99$. Additionally, five data points within the range of $0.05 < P/Po < 0.35$ were collected to calculate the surface areas. The pore size distributions were determined using the desorption isotherm technique.

The nitrogen adsorption surface areas were measured multiple times on identical samples and found to be similar, with a margin of error of ± 5%. This indicates that there was no observed collapse of the small-scale structure due to capillary pressure exerted by the nitrogen.

Figure 4 displays the linear isotherm plot for the Aerogel samples that were created at various final pH levels. The graphs can be divided into two sections, labelled as part (a) and part (b), based on the total amount of adsorbed conductance. Specifically, in part (b), more than 50% of the maximum adsorbed quantity is observed at relative pressures larger than 0.9.

The impact of concluding preparations The pH value, surface area, pore size, and pore volume are depicted in Figure 5. Figure 5 displays the impact of the final preparation pH value on the surface area, pore size, and pore volume.

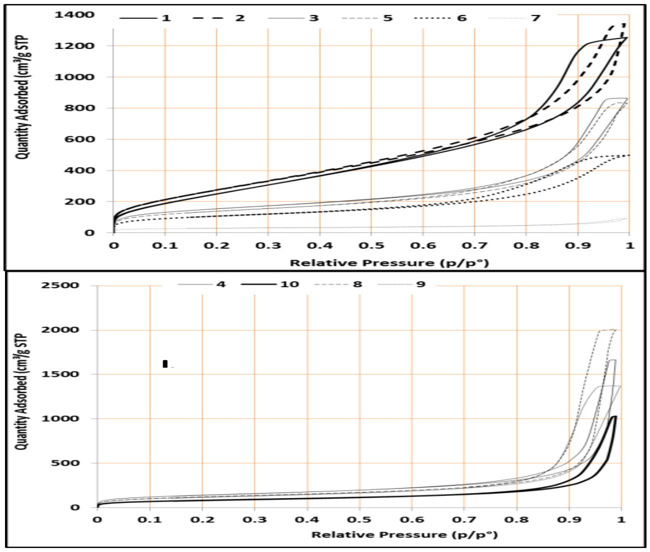

Fig. (4): liner isotherm plot for Aerogel prepared at initial pH values (a) 1, 2. 3. 5, 6 and 7) and (b) 4, 8, 9 and 10.

In general, the surface areas of silica aerogel tend to decrease when the pH value of the final preparation increases, as depicted in Figure 5-a. Figure 5b illustrates the relationship between pore volume and size in relation to the final preparation pH value. It is observed that the porosity virus pH curve exhibits a similar behaviour to that of the pore volume. Two pH values (2 and 8) were found to result in the highest pore volume, but a single maximum was observed at pH 8 for pore size. The manufacture of Aerogel under a neutral environment (pH = 7) is of utmost importance in order to obtain a product with the smallest pore size, pore volume, and surface area

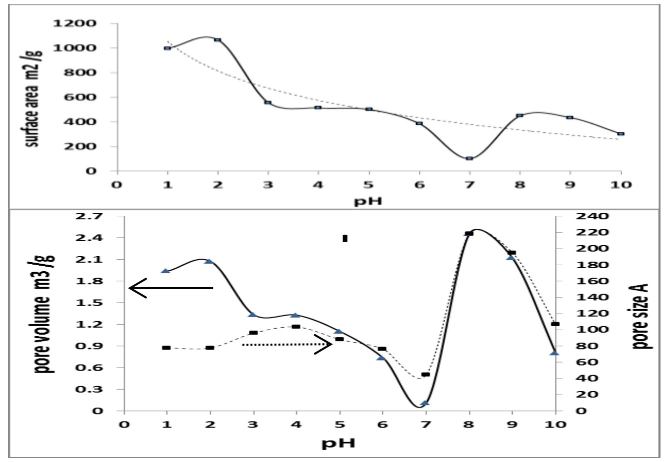

Fig. (5): influence of preparation pH value on (a) surface area (b) pore volume and size.

Additional findings were the graphical representation of t plot, which depicted the exterior surface area, micropore area, and volume. Furthermore, the Langmuir isotherm was visually presented in Figure 6. The data presented in Figure 6(a) demonstrates that Aerogel samples generated at a pH of 7 exhibit the lowest surface area. The micropore volume and area both exhibit a monotonic increase when the pH value increases, following the same approach.

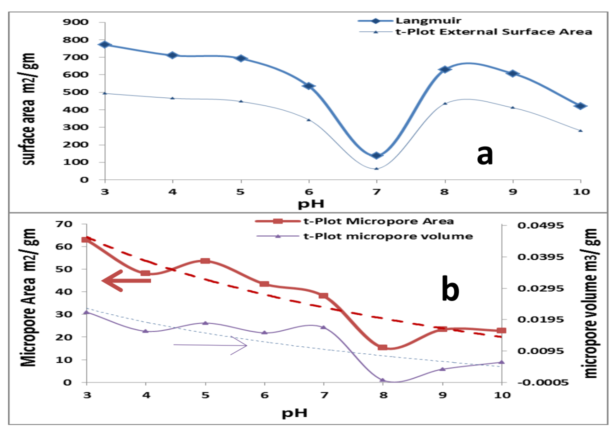

Fig. (6): influence of preparation pH value on, t plot curve, (a) surface area (b) pore volume and size.

Table 1: the nitrogen sorption measurement for silica aerogel											
pH	Sur area				Pore V			Pore size			Porosity %
	single	BET	BJH Ads	BJH Des	single	BJH Ads	BJH Des	BET	BJH Ads	BJH Des	
1	934.186	998.256	1011.09	1105.61	1.93936	1.79503	1.82236	77.7101	71.013	65.931	86.335
2	1009.317	1066.398	987.783	1084.191	2.07515	1.88959	1.93566	77.8378	76.518	71.414	86.987
3	535.0903	556.3385	502.353	540.6836	1.335504	1.334469	1.362222	96.0210	106.257	100.778	82.432
4	493.882	513.7343	482.875	514.913	1.33047	2.60095	2.59059	103.592	215.45	201.24	88.021
5	481.8698	500.9822	477.342	507.3601	1.103551	1.314670	1.306953	88.1110	110.166	103.039	81.360
6	371.39	385.7476	367.544	398.1537	0.735818	0.79273	0.785853	76.3004	86.273	78.95	74.093
7	101.2428	102.1949	53.719	54.0123	0.114741	0.124156	0.123705	44.9106	92.448	91.613	43.759
8	428.5809	450.2661	460.488	552.3212	2.457174	3.116630	3.109947	218.2864	270.724	225.227	90.613
9	413 .858	435.0153	436.353	485.5173	2. 1194	2.131313	2.124917	194.8833	195.375	175.064	87.792
10	289 .199	302.8506	286.478	303.2109	0.8 07021	1.608279	1.602067	106.5900	224.559	211.347	82.383

Table 1 presents a summary of the nitrogen sorption measurement conducted on the silica aerogel samples manufactured at various pH levels ranging from 1 to 10.

3.3. SEM test

Figure 7 presents the scanning electron microscopy (SEM) images depicting various intriguing samples of Aerogel. The photos were chosen based on their pH values, which indicated significant differences during the BET test, in order to analyse the morphology of their pores. These graphics depict various network structures pertaining to the environment in which catalysis preparation takes place.

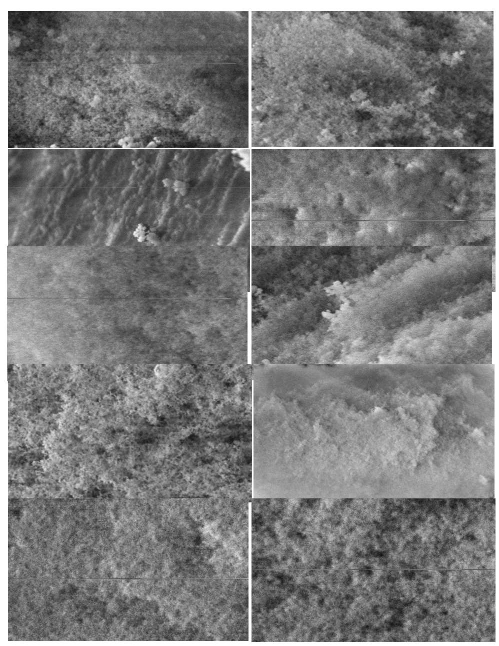

Fig. (7): SEM images for Aerogel samples, pH values are mentioned on the image.

4. Discussion

The preparation of highly translucent Aerogels typically involves a two-step technique. In this study, we employed a single-step procedure to prepare our samples in order to investigate the influence of pH more effectively. Moreover, the current work aims to examine the optical properties of Aerogel solely through the analysis of transmittance spectra, without taking into account small angle X-ray scattering observations.

Given the minimal light absorption of silica across the whole visible spectrum, it can be inferred that the extinction of light primarily occurs owing to scattering. This scattering can be attributed to both bulk scattering resulting from the Aerogel structure and surface defects on the Aerogel [12]. In the context of the Aerogel network, it is observed that the inhomogeneities present within the network are significantly smaller in size compared to the wavelengths of light. As a result, it is anticipated that the scattering of light inside the network will exhibit a nearly isotropic behavior, commonly referred to as Rayleigh scattering.

In addition, all samples of Aerogel were synthesized using the sol-gel technique and derived from a homogeneous material. With the exception of the final pH values, all samples were generated under identical conditions, including reaction temperature, R molar ratio, and aging time. Consequently, the pH values are likely to exert significant effects on the optical characteristics of the Aerogels [13]. The reaction under acid catalysis requires a high electron density, whereas under base catalysis, a low electron density is required. Consequently, the condensation process yields predominantly linear chains in an acidic environment and a more branched network in a basic environment [7].

All samples exclusively comprise silica, therfore, the variance in transmittance shown in Figure 2 may be attributed completely to the unique network structure of Aerogel. The refractive index disparity between the silica network and the pore material (such as air in the case of Aerogel) can potentially serve as a significant cause of light scattering, with the pores functioning as scattering centers.

In general, with the exception of an unusual result observed at pH = 2, it can be observed that as the acidity of the solution lowers, the transmittance of Aerogel also reduces. This decrease in transmittance reaches its minimal value in a neutral environment, namely at pH 7. It is important to note that the hydrolysis reaction exhibits a minimal reaction rate when the pH is equal to 7. At this particular pH, a significant portion of the silica networks remains unreacted. The termination of the electrophilic propensity in the condensation process leads to the alcohol condensation mechanism becoming the preferred mechanism [14]. This condition will result in the formation of highly branched networks, leading to reduced pore diameters and pore volume in the silica material. Consequently, the material will exhibit low transparency. The aforementioned systematic procedure is evident in the corresponding decrease in the pore volume of the Aerogel (as observed in a single test) in relation to the pH value (as shown in table 1). The hypothesized correlation between pH value and transparency was disrupted under the given environmental conditions. In Figure 3, it can be observed that there is a significant rise in the optical transmission of silica aerogel as the pH value is raised from 7 to 8. Nevertheless, it is evident that the proposed association between pore volume and transparency remains valid. This is particularly evident when the pH value exceeds 8, as seen by the data presented in table 1 and Figure 3.

With respect to the peculiar behavior seen in the pH 2 sample, it is widely recognized that this particular pH value corresponds to the silica zero charge point [7]. In other words, the condensation mechanism prior to and after this pH value can be described as electrophilic and electrophobic, respectively. Hence, the decrease in transmission observed in this scenario can be ascribed to similar factors as those observed at pH 7, albeit to a lesser extent.

It should be noticed that the surface area or the pore volume which are determined by applying any of the empirical models are simply approximated values. The BET hypothesis fails to account for surface inhomogeneities and lateral interactions between adsorbates. Hence, it can be inferred that the observed surface area in this technique does not represent an actual interior surface, but rather a distinctive BET surface area. In addition to the measurement of porosity, let us assume that the pores exhibit characteristics of open pore types. In summary, this approach is deemed appropriate for the comparative analysis of materials within a specific series; however, it is advisable to exercise caution when relying solely on the absolute values. Hence, the BET approach can be employed with considerable precision.

The Aerogels samples, which were made using various pH values, demonstrate type-IV adsorption isotherms, as depicted in Figure 1.The aforementioned findings are seen as indicative of the existence of mesoporous materials [13].

The isotherm graphs depicted in Figure 4 can be analyzed using the IUPAC categorization hysteresis loops shown in Figure 1. The pH values of the samples, namely pH 1, 2, 3, and 5 as shown in Figure 4-a, can be categorized as H3 type. Non-rigid aggregates of plate-like particles with slit-shaped pores are characteristic of this category. The samples with a pH value of 6 and 7, as shown in Figure 4-a, can be categorized as H4 type due to their plot characteristics, which are indicative of narrow slit holes, including pores within the micropore range. The plots corresponding to pH values of 4, 8, 9, and 10 in Figure 4-b can be categorized as H1 type, which refers to the presence of clearly defined cylindrical pore channels [11]. With the exception of the pH 4 Aerogel sample, the mechanism responsible for generating a linear isotherm plot can be categorized into two branches: acidic and basic behavior. In an acidic environment, the formation of slit-shaped holes is observed, but in a basic environment, the predominant pore channels have well-defined cylindrical structures.

With reference to Table 1, it is evident that with a pH of 4, the pore volume and pore size, as determined by BJH adsorption and desorption techniques (representing the cumulative volume of pores and average pore diameter), exhibited values that deviated from the information provided in the table. This observation is further supported by Figure 5-b.This behavior can be explained as follows: at a pH of around 4 (specifically 4.5 for silica), referred to as the isoelectric point (IEP), where the zeta potential is equal to zero, the rate of condensation reaction reaches its minimal value. Therefore, the mechanism of water condensation will be advantageous [14-17]. This phenomenon has the potential to result in networks with fewer branches, leading to larger pore diameters and hence enabling a significant increase in adsorption capacity at high relative pressures.

The scanning electron microscopy (SEM) images of samples with pH values of 2 and 8 exhibited a broad variation of pore sizes, together with a significant volume of big pores, as determined by the Brunauer-Emmett-Teller (BET) test. The results indicate that the pH 8 sample had a higher propensity for closed pore creation compared to the pH 2 sample. This characteristic was evident in the corresponding surface areas of the samples. Table 1. Samples with different pH values exhibit a restricted spectrum of pore sizes. In an acidic environment, these samples display softened characteristics, while in a basic environment, they exhibit strongly branching features, perhaps including closed pores.

Conclusions

The optical transmittance of the prepared silica was measured. The pH levels during the initial preparation of aerogels have a significant impact on their properties. The BET test, when combined with other methodologies, can offer a systematic approach for quantifying the structure of Aerogels networks throughout inquiry. To enhance the production of the materials with a significant surface area, the incorporation of catalysts is recommended through the utilization of sol-gel formulations. In general, an environment with higher acidity tends to result in the production of Aerogels with a greater surface area, while an environment with more basicity leads to the formation of Aerogels with a smaller surface area. The pore volume of aerogel exhibited a consistent trend, similar to that of surface area, in relation to the preparation parameter. The correlation between porosity and pore size, as well as the influence of pretreatment pH values, exhibits a greater degree of irregularity. Hence, in order to customize the desired structural characteristics, such as pore size and surface area porosity, it is crucial to carefully choose the initial pH value based on the specific type of Aerogel structure employed.

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