The influence of various pH values on the aerogel physical properties by sol-gel technique

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Abstract

Hydrophobic silica aerogels were successfully preparation by an ambient pressure drying method from sodium silicate (Na_2SiO_3) with different pH values (5, 6, 7, 8, 9 and 10). In this study, acidic HCl (1M), a basic NH_4OH (1M) were selected as a catalyst to perform the surface modification in a TMCS (trimethylchlorosilane) solution. The surface chemical modification of the aerogels was assured by the Fourier transform infrared (FTIR) spectroscopic studies. Other physical properties, such as pore volume and pore size and specific surface area were determined by Brunauer-Emmett- Teller (BET) method. The effect of pH values on the bulk density of aerogel. The sol–gel parameter pH value in the sol, have marked effects on the physical properties of the silica aerogels produced by this technique. The density and the hydrophobic tendency of the aerogels were significantly influenced.

تأثير قيم pH المختلفة على الخصائص الفيزيائية للأيروجل بواسطة تقنية سول-جل

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الخلاصة

تم تحضير سيليكا ايروجل بنجاح بواسطة طريقة تجفيف الضغط المحيط من سيليكات الصوديوم (Na_2SiO_3) مع قيم مختلفة من الدالة الحامضية pH (5، 6، 7، 8، 9 و10). في هذه الدراسة، قمنا باختيار حمض الهيدروكلوريكHCl (M1)، هيدروكسيد الأمونيوم NH_4OH القاعدية (M1) كمحفزات، وقام بإجراء تعديل السطح بواسطة محلول (trimethylchlorosilane) TMCS، وتم تأكيد التعديل الكيميائي السطحي لعينات الايروجل بواسطة دراسة طيف تحويل فورير للأشعة تحت الحمراء (FTIR). تم تحديد الخصائص الفيزيائية الأخرى، مثل حجم المسام ومساحة سطحه بواسطة طريقة بروناور-إيميت-تيلر (BET). تم إثبات تأثير قيم الأس الهيدروجيني على الكثافة الظاهرية لعينات الايروجل المعدة. إن قيمة الرقم الهيدروجيني لمعلمة sol-gel في sol، لها تأثيرات ملحوظة على الخواص الفيزيائية لعينات الايروجل التي تنتجها بهذه التقنية. كانت الكثافة والنزعة الكارهة للماء تتأثر بشكل كبير.

Introduction

Since its discovery by Kistler in 1931[1], silica aerogels are advanced materials and are new in the field of materials science. Silicate aerogels consist of 4% of a weak structure from the matrix of silicon dioxide, the residual 96 % is air. So that is one of the lightest weight solids Absolutely [2, 3]. An aerogel is made by the so called "sol gel Technique" with remove the Solutions from a gel without a significant shrinkage and without pore collapse [4]. Commonly, the starting point of the sol formation is the mixing of precursors e.g. Tetraethylorthosilicate TEOS, Tetramethylorthosilicate TMOS, and

sodium silicate (Na_2SiO_3), which are considered to be historical the first significant precursor [1, 4]. It is the inorganic matter that easily dissolves in distilled water due to the polar property of the molecules Si-O and Na ion. The polar Property of the molecule (Si–O and Na^+ ion) on one hand makes it dissolve readily in water. In addition to, it is easy to handle and poses no flammability danger like silicon alkoxides, and it is chemically long-range stable under standard conditions of use and stockpiling [4]. The sodium silicate interacts with an acid such as HCl as shown in the Eq.(1).

$$Na_2SiO_3 + 2HCl + H_2O \rightarrow Si(OH)_4 + 2NaCl \tag{1}$$
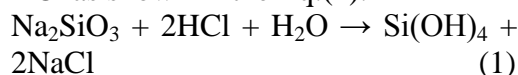
A salt is created, which must be removed by was by used ion exchange column [5]. After that, the hydrolyzed silicate links together forming siloxane bridges.

$$\equiv Si\text{-}OH + HO\text{-}Si \equiv \leftrightarrow \equiv Si\text{-}O\text{-}Si \equiv + H_2O \tag{2}$$
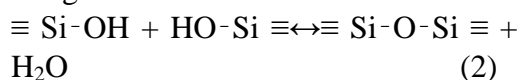
Usually, silica aerogels were created by supercritical drying (SCD) process so as to attain a porous structure [6, 7]. The (SCD) can avert capillary stress Which causes shrinkage. However, the (SCD) process is so expensive and dangerous that real practicality and commercialization are hard [8]. Thus, last few years, preparation hydrophobic silica aerogels by an Ambient Pressure Drying (APD) technique has been attracting great interest. Silica aerogels could be successfully preparation by (APD), through solvent exchange and surface modification of the wet gel using trimethylchlorosilane (TMCS), ethanol (EtOH), hexane mixed solution before drying [9]. silica gel and the synthesis of silica aerogel [10]. Because of the characteristic properties and the unique for hydrophobic aerogels make it an attractive material for a multiplicity of applications such as liquid propellant transporters, highly effective catalysts, and radiators in Cherenkov detectors for high energy particles, filters for automobile exhaust systems and industrial pollutants, heat storage devices for automobile, encapsulation media, hydrogen fuel storage composite and oil spilling clean-up [3, 4 and 11].

Methods
1. Raw materials

Material	Chemical formula	Equip with	Purity
waterglass (sodium silicate) solution	$Na_2O{:}SiO_2$	Sigma- Aldrich	
hydrochloric	HCl	AMERCO	99.0%
Ammonium Hydroxide	NH_4OH	AMERCO	96.0%
Trimethylchlorosilane(TMCS)	$(CH_3)_3SiCl$	TCI Japan	> 98.0%
Ethyl alcohol	C_2H_5OH	Sigma- Aldrich	> 98.0%
n-Hexane	C_6H_{14}	Sigma- Aldrich	> 98.0

2. Procedure

The basic step in the preparation of silicic acid Si $(OH)_4$ from a sodium silicate solution (Na_2SiO_3) based by removing sodium ions, this can be attained by adding hydrochloric acid (HCl) to the sodium silicate until the pH of the solution became 7. The chemical reaction was described in Eq.(1).
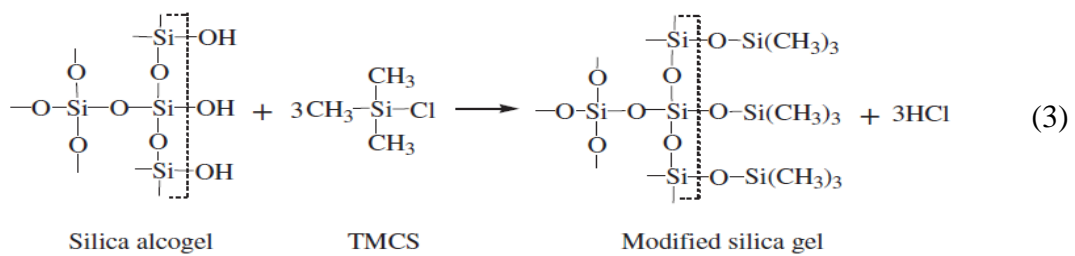
It is clear from Eq.(1) that NaCl salt is the byproduct of this reaction. The

NaCl could be taken away by passing the solution through an ion exchange column to replace Na^+ ions in the solution by hydrogen ions H^+. Silicic acid sol was obtained at pH 2.2.

Through this work, six samples of hydrophobic silica aerogels had been prepared at different sol pH values, 5, 6, 7, 8, 9 and 10. This was achieved by adding drops of NH_4OH (1N) as catalysis to 10 ml of silicic acid until the pH is adjusted to the pre-mentioned values, with continuous stirring using the magnetic stirrer. The gel time was different for each sample depending on the pH value. The samples then were soaked in a distilled water for aging for two hours, in this case, the gel is called a wet gel. The gel samples were then soaked in EtOH, that replaced with fresh EtOH four times in a period of four hours, in order to complete the aging process and to reduce surface tension, the gel then called (alcogel).

Hexane is then added until the alcogel is fully immersed, then the EtOH is extracted from the gel as separated solution in the bottom of the beaker. This process is repeated 4 times within 12 hours, in order to completely remove EtOH, and replaced by hexane. The other step is to modification of the surface by soaking the alcogel into a mixture of hexane and TMCS at the ratio of 10: 0.2 ml. This operation has lasted 12 hours. Utilizing hexane instate of EtOH because hexane does not interact with TMCS and possesses relatively weak surface tension. The modification process by TMCS is given by the following Eq.(3) [12].

$$\text{Silica alcogel} \quad + \quad 3CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{Si}}-Cl \quad \longrightarrow \quad \text{Modified silica gel} \quad + \quad 3HCl \qquad (3)$$

Silica alcogel   TMCS   Modified silica gel

The last step is to remove the non-reactive TMCS and hydrochloric acid, by using pure hexane and this process were repeated 3 times during a period of 6 hours. All of the above steps were done at 50 $^\circ$C. The aerogel samples then became ready for the drying process. The drying step starts at 50 $^\circ$C via an increase of temperature by10 $^\circ$C every half hour until it reaches 120 $^\circ$C. Then the samples were left for 2 days at this temperature. Fig.1 shows the flow chart of the aerogel preparation steps.
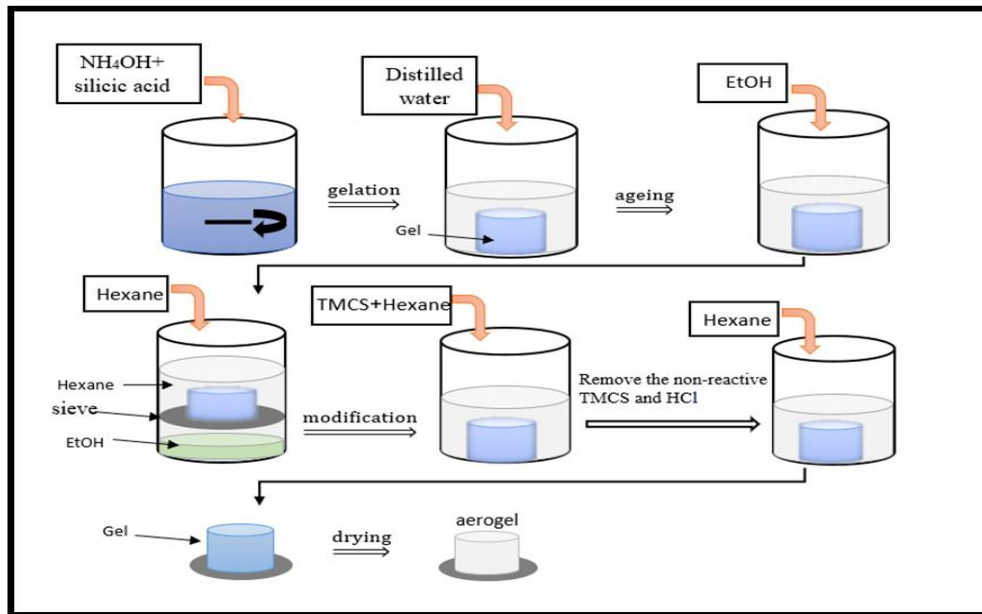
Fig.1: Schematic chart for the systematic preparation of hydrophobic silica Aerogels.

Characterization

The surface modification was confirmed with the Fourier transform infrared spectroscopy (FTIR) The recording range was (400–4000) cm^{-1} using KBr pellets, (Shimadzu-8400S) supplied from the company of thermos scientific (USA).

Mean pore size, pore volume, and the surface area were confirmed by Brunauer–Emmett–Teller (BET) method (BEL, JAPAN) from the amount of N_2 gas adsorbed at various partial pressures.

Results and discussion

Commonly, FTIR spectra are analytic qualitatively, but it is possible to compare the intensity of specific bonds in order to give a quantitative perception [13]. Though the recorded FTIR spectra, all samples reflect similar features. The similarity among the spectra indicates that there is no significant chemical change in the silica aerogel that prepared under different pH. However, there are some differences in the relative intensity of some vibration bonds. This may be due to the injection of the organic modifiers into the silica structure. This organic rout can be used as a referee factor in the determination of the hydrophobic properties of the aerogel. As well as, it was found that these differences also depend on the pH values of the samples. Fig.2 illustrates the FTIR spectra for six samples of silica aerogel samples that prepared at pH of 5, 6, and 7 in Fig.2a, and at pH of 8, 9 and 10in Fig.2b.
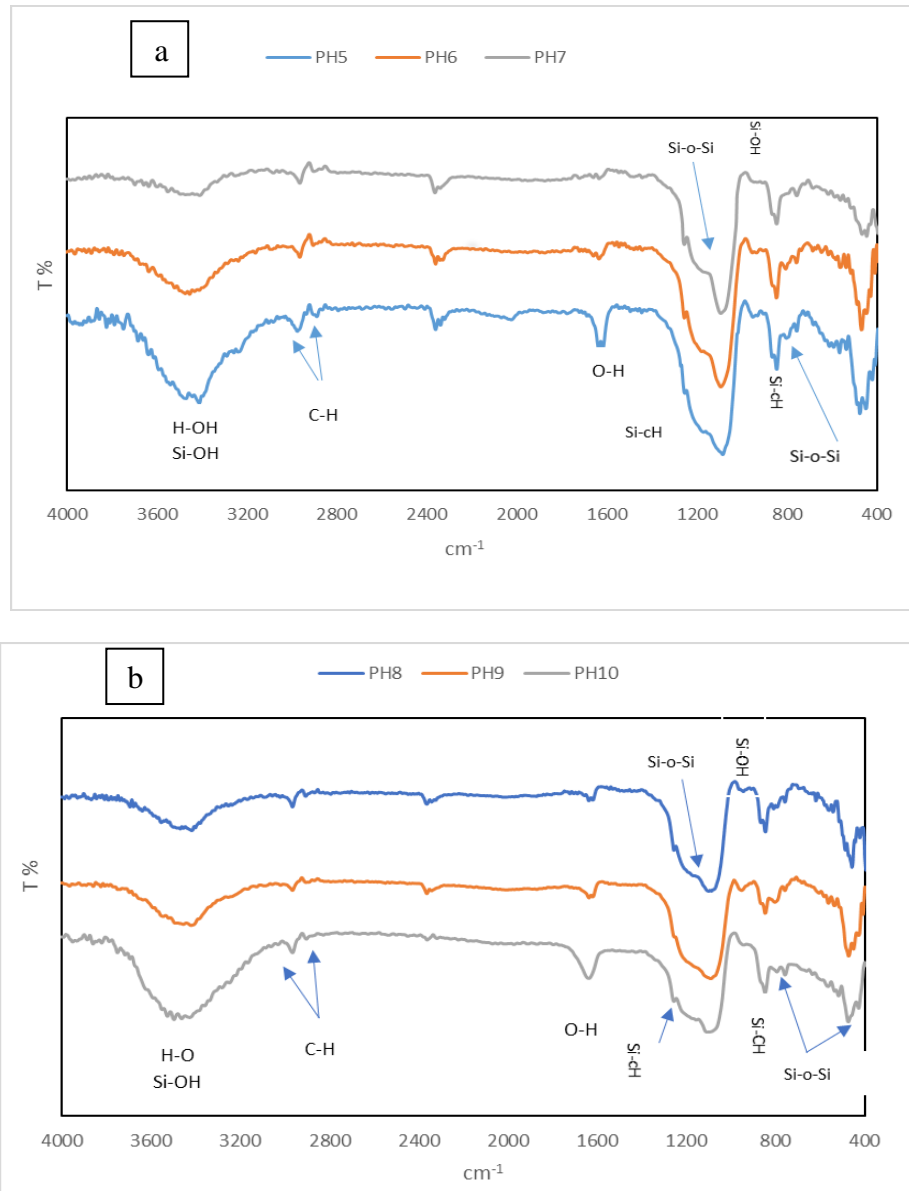
Fig.2: FTIR spectra of the aerogel at different pH. a-for pH 5, 6 and 7 b-for pH 8, 9 and 10.

A number of methyl vibrations modes CH_3 are present in these FTIR spectra, Fig.2, where two weak bands are located at 2962 cm^{-1}, 2900 cm^{-1}, which are clearly stronger in the case of TMCS modified aerogels [14]. Also, a small peak is present at 1261 cm^{-1} as well as a weak peak centered at 848 cm^{-1}, these bands may correspond to vibrations CH_3 that are associated with Si, (Si-CH) [15]. All of the above shows indicated the successful introduction of the hydrophobic organic group into the silica network.

In case of samples of pH5, pH 6, and pH 7, the intensity of the peaks located at 2962cm$^{-1,}$ 2900cm^{-1}, 1261cm^{-1}, and 848cm^{-1}, which are related to C-H bond, were increased as the pH value increases. As well as the O-H peak intensities at 3410 cm^{-1}, 1639 cm^{-1} and 960 cm^{-1} were relatively reduced with the pH increasing. The increase in the C-H peak intensity and the weakness at the O-H peak intensity may indicate to the hydrophobicity enhancing. The above was due, at pH 5 of the silicic acid solution, the

hydrogen ion concentration was high which caused to attack the Si-O bond, boosting the hydrolysis reaction, so that, the hydrolysis reaction rate of silicic acid solution was much higher than the condensation. Consequently, there were smaller hydrolyzed Si $(OH)_4$ monomers in the gel. This resulted in a small pore volume. Furthermore, it the large size of TMCS, the efficiency of the surface modification process would be low.

At pH 6, the rate of hydrolysis and condensation reactions reached to equilibrium [16, 17]. While the pH value above 6, the reaction equilibrium moving towards to form polymers. In this state, the reaction rate is quick to form the homogeneous and high cross-linked network structure, leading to the decreases the specific surface area of the aerogel.

There was a turning point when the pH moved to basal value (8, 9 and 10). The increase in peak intensity of O-H bonds decreases in C-H, causing a decrease in hydrophobicity. This is due to increased addition (NH_4-OH), which increases the rate of O-H in the structure of aerogel. Causing a reduced modification process efficiency even if the aerogel network was of high pore size.

Fig.3, demonstrates the variation of pore volume and size with preparation pH calculated by BET methods, and it appears that pore volume and size exhibit similar behavior with respect to pH, each has a maximum at pH = 7. It is notable that the preparation of aerogel under neutral conditions yields the largest pore size, pore volume.
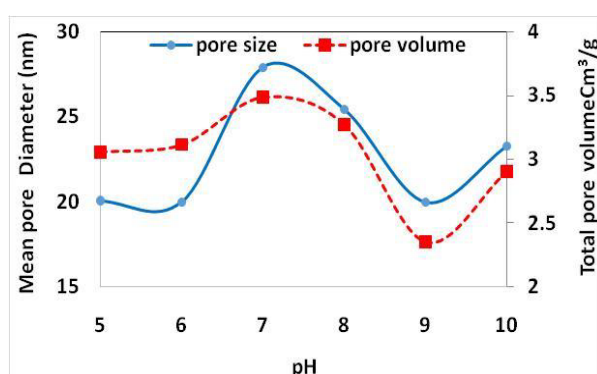

Fig.3: Influence of pH on pore volume and pore size.

Table 1 summarizes the nitrogen adsorption-desorption isotherms measurements at 77 K for silica aerogels prepared under pH =5-10. These measurements are utilized through BET methods was included;

the main pore diameter in (nm), a specific surface area in cm^2/g, and total pore volume in cm^3/g, It was also recorded bulk density of each sample about the pH values.

Table 1: The N_2 adsorption–desorption isotherms measurements at 77 K for silica aerogels prepared under pH =5–10.

pH	Mean pore Diameter (nm)	Specific surface Area cm^2/g	Total pore Volume cm^3/g	bulk density g/cm^3
5	20.031	610.09	3.0552	0.070714
6	20.011	623.00	3.1168	0.069727
7	27.923	499.15	3.4844	0.118375
8	25.434	514.43	3.2710	0.11122
9	19.990	470.58	2.3517	0.180139
10	23.314	497.83	2.9016	0.135529

Conclusion

The starting pH value played important on the structural and physical properties of the aerogel samples. Where the pH value appears to have an effected on the surface modification process which is shown by the results of the FTIR examination. The pore volume and size formed through the sol-gel process were very affected by the pH environment. At pH7 give the best results such as high surface area.

The pH value had an effect on the bulk density of the aerogel. The best value for the apparent density was at pH 6.

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