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Influence of reactant catalyst type and Drying Control Chemical Additives (DCCA) on optical and structural properties of silica aerogel prepared via ambient pressure drying

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Abstract

We have studied the synthesis environment of ambient pressure silica aerogels influence on their resulting morphological and optical properties. Transparent nanoporous silica aerogel was synthesized at ambient pressure using tetraethylorthosilicate precursor via a sol-gel process. Effect of drying control chemical additives and catalyst on physical properties was investigated. Trimethylchlorolsilane was employed as a hydrophobic reagent in the surface modification process. All aerogel samples were prepared utilizing a subcritical procedure under reactant pH fixed at 8.3, using just ammonium hydroxide or together with ammonium fluoride as catalyst. The effects catalyst types as well as drying control chemical additives on the physical properties of the nanoporous silica aerogels (particle size, surface area, percentage of shrinkage, contact angle, and density) were investigated.

Keyword: Silica aerogels, Hydrophobic, Silylating Agent, Contact angle, Ambient Pressure.

تأثير نوع العامل المساعد والإضافات الكيميائية المسيطرة على التجفيف على المواصفات البصرية والتركيبية لمادة الايروجل المحضر تحت الضغط المحيط

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الخلاصة

تم دراسة تأثير وسط التحضير لمادة الايروجل المحضرة تحت الضغط الجوي .على الخواص التشكيلية والبصرية ،تم تحضير السيليكا ايروجل ذات المسامات النانويه تحت الضغط الجوي باستخدام البادره تترااثيل اورثوسيليكات وبطريقة السول جل . تم التحقق من تأثير الإضافات الكيمائية والعوامل المساعدة على الخواص الفيزيائية ،وقد استخدُم تيراثيل كلوروسيلان كجذر طارد للماء في عملية تحسين السطح . جميع عينات الايروجل حُضرت باستخدام إجراءات تحت الحرجة وبثبوت مقياس الحامضيه (PH) على 8.3 وباستخدام هيدروكسيد الامونيوم فقط تارة ومع فلوريد الامونيوم تارة أخرى كعوامل مساعده. ان تاثيرات نوع العوامل المساعدة والإضافات الكيميائية على الخواص الفيزيائية للايروجل ذات المسامات النانوية (حجم الجسيمات، المساحة السطحية، النسبه المئويه للانكماش ، زاوية الالتصاق، والكثافة) تم التحقق منها.

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Introduction

Silica aerogels are porous ceramic materials including high surface area (500–1000 m^2/g), high porosity (80–99.8%), low bulk density (0.003–0.8 g/cm^3), and low thermal conductivity (~0.02W/m.K) [1, 2]. It is ever conceived one of the lightest weight solids [3]. Because of their unique nanostructures, aerogels show low density, high porosity and high surface area and have been widely used in many fields, such as thermal insulation, catalysts [4, 5], acoustic insulation, , super-thermal insulators, chemical sensors , solar thermal devices, [6, 7] catalyst carriers, drug delivery and sensors[8]. The hydrophilicity is the inherently of silica aerogel in nature. The hydrophilic property of it led to limit their use in long term applications because they absorb surrounding moisture from the sticky environment [9]. The unmodified surface of silica aerogel carries 4–6 hydrolyzable silanol (Si-OH) groups per nm^2, on an average and therefore, the surface exhibits hydrophilic property [10]. It is essential to tune the surface free energy of silica aerogel surface such that the organic non-polar liquid wet the aerogel surface fully and get easily absorbed and at the same time the surface is non wetable for polar solvents like water that have high surface tension values [11]. One can achieve hydrophobic silica aerogels either by using the surface modification or by the derivatization method [12]. it can be reduced the apparent unmodofied surface of silica aerogels by using silylating which can be replace the surface polar –OH groups by non-polar –CH3 or HCL groups [13]. In order to have such a hydrophobic property in the material, the solid–liquid interfacial energy should be greater than that of the solid–vapour interfacial energy, as given by the Young’s equation [14]

$$\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos\theta$$

Where γ_{SV}, γ_{SL} and γ_{LV} are solid–vapour, solid–liquid and liquid–vapour interfacial energies, respectively, and (θ) is the contact angle. Hydrophobic aerogels can be used as self-cleaning coatings in buildings and constructions[15]. Feasibilities of using hydrophobic aerogels for oil spill clean-up and for surface protection of structure from corrosion of the environment have been proved [16]. Surface modification with hydrophobic properties using the sol–gel method has been investigated during the recent years. Davis et al. have investigated the effect of exchanging water and ethanol with the initial pore fluid. Gels aged in and dried from water exhibit surface areas on the order of 1000 m^2/g immediately before drying and 500 m^2/g after drying, whereas those washed and aged in ethanol exhibit surface areas on the order of 2000 m^2/g prior to and 1000 m^2/g after drying. This effect was found to be reversible and the final pore fluid was the dominant factor in the xerogel surface area [17]. Tadanaga et al. reported the formation of transparent superhydrophobic films on glass plates through the sol–gel method by the combination of microstructural and chemical approaches they found that The contact angle for water in the films was 165° and the transmittance for visible light was higher than 92%. A roughness of 20 to 50 nm was obtained, which is too small to scatter visible light [18]. K. Balkis Ameen et al. study the effect of heat-treatment on the physico-chemical properties of silica aerogel prepared by sub-critical drying technique they found that when heat-treated to 900º C, the average pore diameter decreased from 56 to 50 A°. The reduction in the surface area and an increase in the silica particle size were attributed to the sintering process and aggregation of primary silica particles[19]. D.B. Mahadik and some researchers demonstrate Effect of concentration of trimethylchlorosilane (TMCS) and hexamethyldisilazane (HMDZ) silylating agents on surface free energy of silica aerogels they found that that the surface free energy of aerogels can be tuned in wide range from 5.5892 to 0.3073 mJ/m^2 by modifying their surface using TMCS and HMDZ silylating reagents[20] . In this paper, we study the influence of reactant catalyst type and Drying Control Chemical Additives (DCCA) on microstructure, density and optical transmittance in silica aerogels prepared via ambient pressure drying technique.

Experimental

Materials

The chemicals used in the synthesis were, tetraethylorthosilicate (TEOS) (with> 99.0% purity), provided from Sigma-Aldrich (Germany), spectroscopic grade ethyl alcohol (200 proof > 99.5% purity), TMCS(Trimethylchlorosilan) C_3H_9ClSi, Molecular Weight(108.64), > 98.0%(GC), provided from TCI Japan, N,N,dimethaylformamide (C3H7NO)> 99.0% purity) deionized water catalyzed by ammonium fluoride(> 98.0% purity) all supplied from Sigma Aldrich. Deionized water was catalyzed by hydrochloric acid (0.15 M,> 99.0% purity, AMERCO) and by ammonium hydroxide (28-30% concentration, BDH), n-Hexane with> 98.0% purity), provided from Sigma-Aldrich (Germany).

Procedure

Silica gels were prepared via a two-step procedure as following; TEOS, ethanol, water, and hydrochloric acid, molar ratio (1:8.6:1.2) were mixed to form condense silica solution. NH4OH solutions were heated under magnetic stirring at 303 K for 15 min. Then 0.5 mℓ of C_3H_7NO, was added as (DCCA) and left for further 1 hour under magnetic stirring. The resulting sol was allowed to gel in 1.35 cm diameter plastic tubes and then aged in the same tubes for 24h at 60° C. In order to remove any unreacted monomer from the gel network, the gels were washed with pure ethanol in five 24 h steps, using fresh ethanol for each successive step. After washing in ethanol prepared (ethanol-Hexane) solution to modified the inner structure of gel, the gel wished in (ethanol-Hexane) solution in four 48h. After above steps it's prepare solution (TMCS+Hexane) the procedures as following:

a. Add TMCS solution and take the gel in sealed and heat container with gel and TMCS solution to 60° C for 24 hr.
b. Allow the container to cool to room temperature.
c. Exchange the TMCS solution with fresh TMCS solution.
d. Heat container to 60° C with gel and TMCS solution for 24h.
e. Repeat b and c
f. Repeat a and b
g. Exchange the gel with fresh hexane 3 more times for 24h. in every addition.
h. Place the gel to dry out over the course of 1-2 days and Place the gel in oven at 140°C for 2 hr.

Characterization of aerogels

UV-VIS spectrophotometer (Ultrospec. 4300 pro) was used in this work to record the transmittance of the aerogel samples. The average transmittance for each curve was calculated by numerically integrating the area under the transmittance curve over the visible range of light (400 nm - 700 nm).By weighing cylindrical samples of known dimensions; the apparent densities of aerogels were calculated. The samples were also characterized by Fourier transform infrared spectroscopy (FTIR) (model Irpresting-21, Supplied by Shimadzu), which gave information about various chemical bonds responsible for hydrophobicity, such as O–H, Si–C, and Si–O–Si.

The morphology and microstructure of silica aerogel samples were observed by scanning electron microscopy (SEM, ULTRA 60) in secondary electron mode. The specific surface area of aerogel samples were determined by the BET method (Micromeritics ASAP 2020). Bulk density of the dried gels, it was calculated by measuring their mass and volume, the volume of aerogel was calculated using $V = \pi R^2 h$, where R^2 is reduce and h is high of the aerogel. If "m" is the mass of the aerogel then the bulk density = m/V. the percentage of shrinkage (V %) was calculated from the change in the volumes of the alcogel and the aerogel using the formula:

$$\left[1 - \frac{V1}{V2}\right] * 100\%$$

where V_1, V_2 are the volume of the aerogel and alcogel. Hydrophobic properties was estimated by measuring the contact angle of a water droplet on the samples using contact angle system.

Results and discussion

Figure- 1 show the absorption spectra (transmittance vs. wavelength) of aerogel with different catalysis, inside figure the mark All refer to addition of (NH_4OH+NH_4F+DCCA), OH+F refer to addition of (NH_4OH+NH_4F), while OH refer to addition (OH) only as catalysis. It's clear from fig. when add all catalysis (NH_4OH+NH_4F+DCCA) the transmissions is high compare with another catalysis in the same wave length.

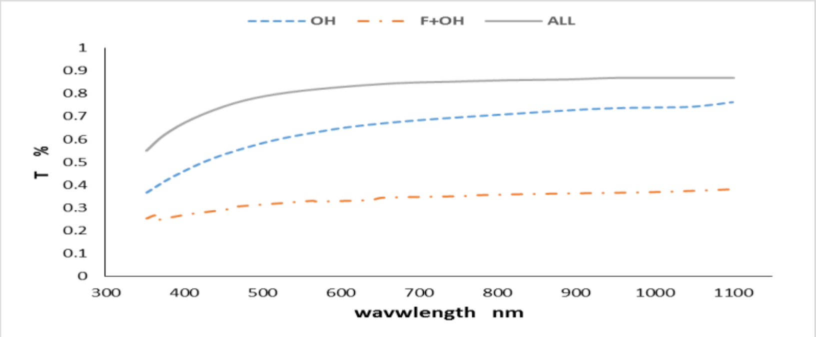


Figure 1- the relation between transmittance vs. wavelength with different catalysis.

The FTIR studies were based aerogels, as shown in Figure-2 the broad band at around 3400 cm^{-1} and the peak at around 1600 cm^{-1} are due to O–H groups. The peaks at around 1100, 800 and 470 cm^{-1} are due to asymmetric, symmetric and the bending modes of SiO_2. The peaks at 1260, 840 cm^{-1} related to the Si–C bonds and 2980, 1450 cm^{-1} related to C–H bonds the intensity of the peaks related to –OH at 3400 and 1600 cm^{-1} decreased with the addition of the silylating agent. The residual Si–OH groups are the main source of hydrophobicity of the aerogels. It can be seen from the Figure- 2 that with the increase of alkyl groups, the intensity of the C–H absorption peaks increase, clearly indicating the replacement of surface H from the Si–OH by the nonhydrolizable Si–R3 groups resulting higher hydrophobicity.

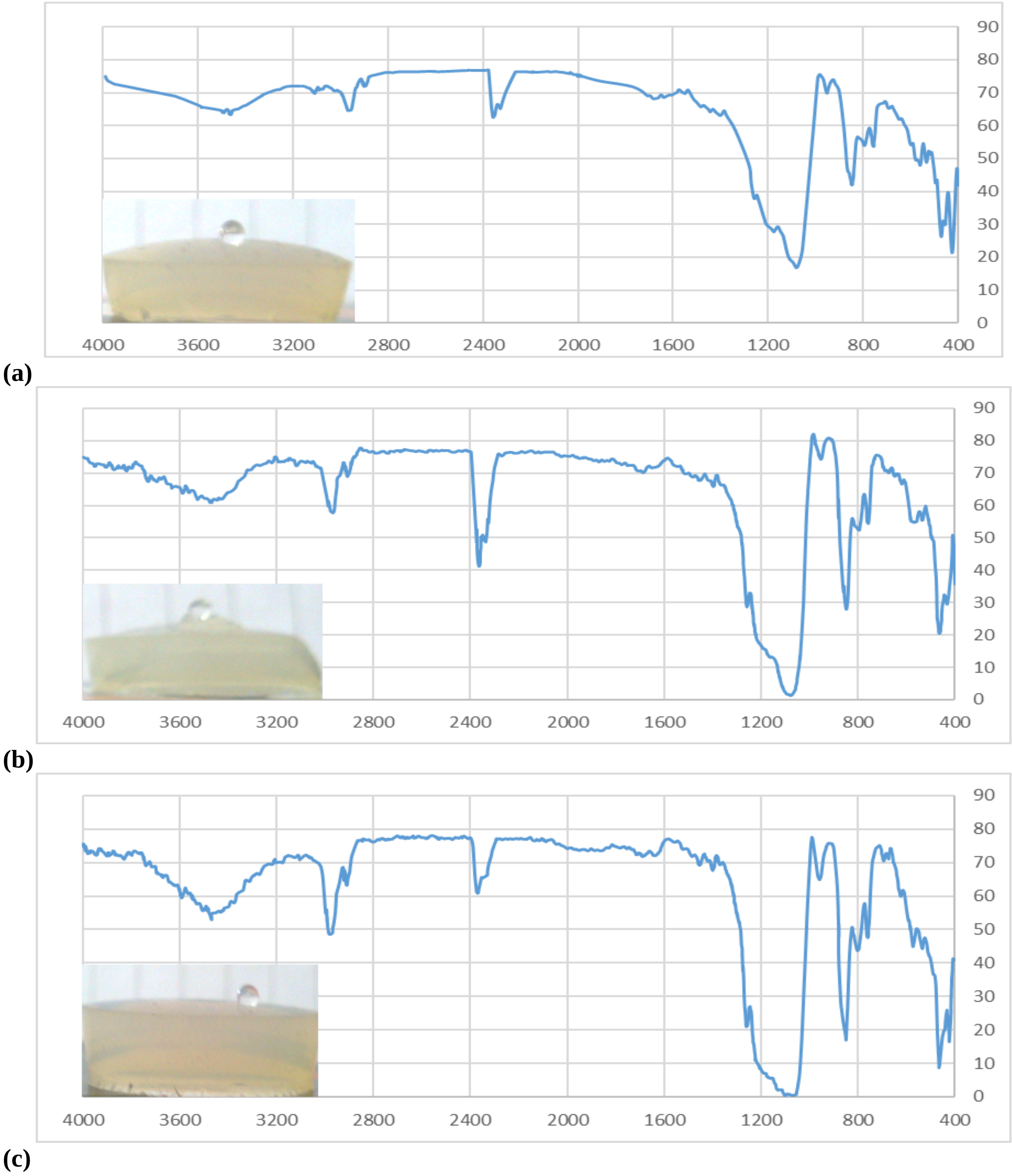


Figure 2- FTIR of aerogel: (a) with NH_4OH, (b) with NH_4OH+NH_4F (c) with $NH_4OH+NH_4F+DCCA$

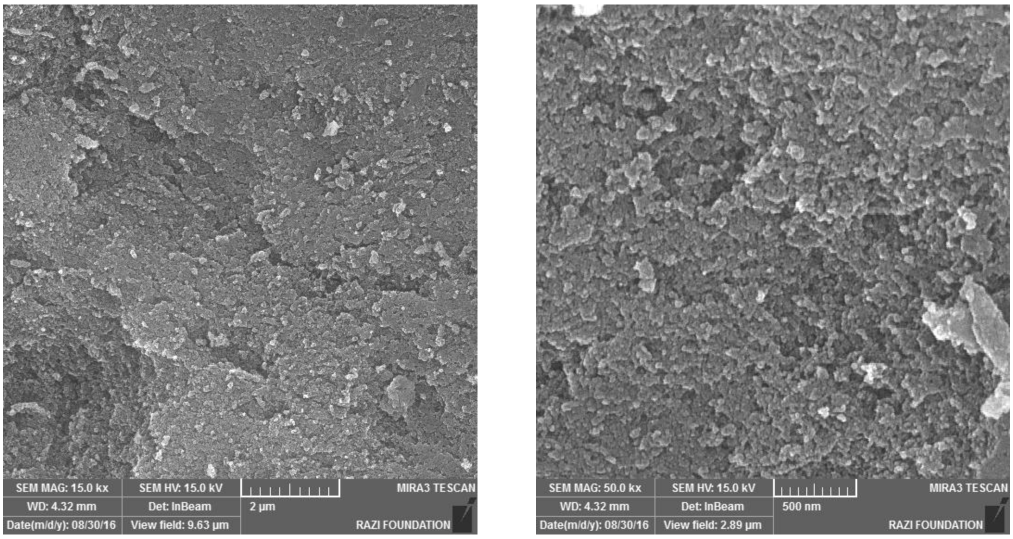
Table- 1 indicate some of parameters such as surface area, percentage of shrinkage, contact angle, density, and piratical size :- From this table we observe that the density and the shrinkage is little in case of addition NH_4OH only as well as we find the contact angel (the degree of hydrophobicity) is large compare with case two and three.

Table 1- Physical and hydrophobic properties of the silica aerogels with different catalysis

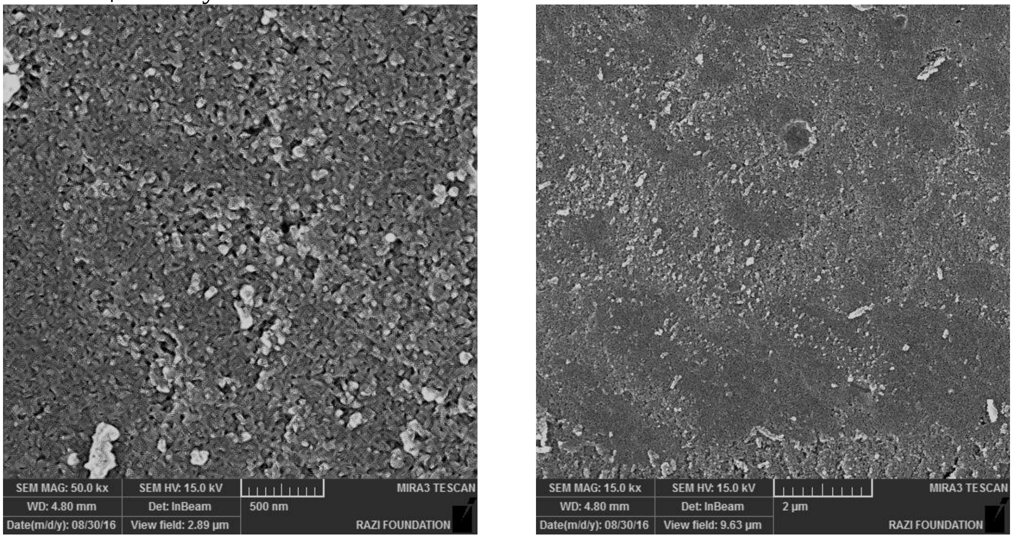
	$NH_4OH+NH_4F+DCCA$	NH_4OH+NH_4F	NH_4OH
Surface area (m^2/gm.)	357	190	294
Contact angle θ	129.11	130.35	135.64
Volume of aerogel before drying(cm^3) After drying(cm^3)	5 1.57	5 2.07	5 2.27
Shrinkage %	68.6	58.6	55.6
Density(gm./cm^3)	0.31	0.29	0.25
Particle size (nm)	19	21	16

SEM observations

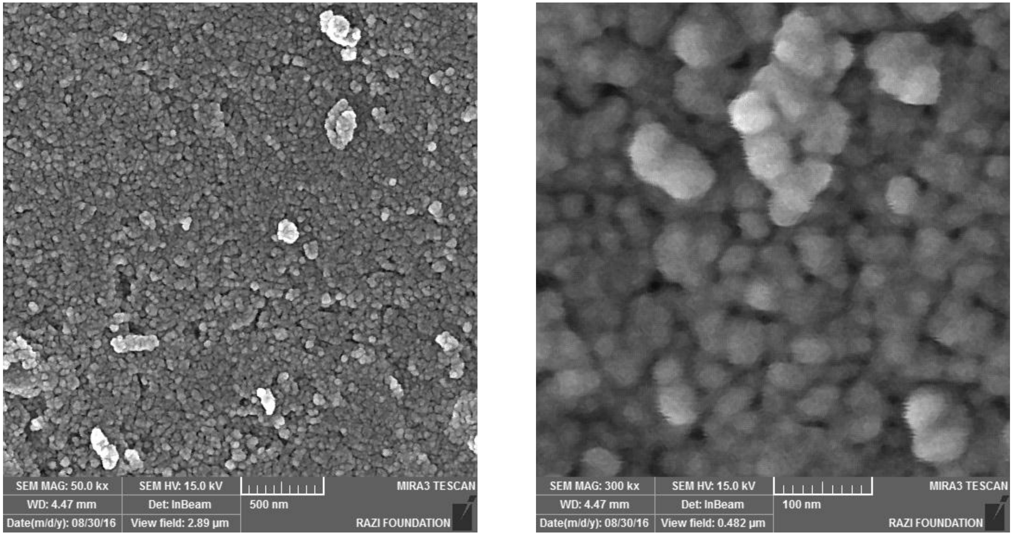
Scanning electron microscopy of the aerogel specimens demonstrates the striking differences in nanostructure which are available with different catalysis (see Figure- 3). Here it becomes apparent that the catalysis plays the most significant role in directing the morphological habit of the aerogel structure, although the solvent, precursors and another environments are conforming. It's clear from SEM image that the samples with NH_4OH only, the particles aggregated and has slimmer particle size compared while the second samples (NH_4OH+NH_4F) which clear more homogenous and has larger particle size, for addition ($NH_4OH+NH_4F+DCCA$) the structure of aerogel is difference, the particles is separated from each other's and the aggregation of it is decrease compared with the two another samples.



with NH_4OH only



with NH_4OH+NH_4F



with $NH_4OH+NH_4F+DCCA$

Figure 3- SEM images of aerogel with different catalysis.

with NH_4OH only

with NH_4OH+NH_4F

with $NH_4OH+NH_4F+DCCA$

Figure 4- Photo of silica aerogel with different catalysis.

In addition to catalysis effected on geometrical shape of silica aerogel as shown in Figure -4, the using of NH_4OH only it leads to get cracks due to the lack of control over the process of evaporation of the liquid, which increases surface tension within the pores and as a result get broken in the internal structure of the network, and this leads to notable for cracks, in case of addition NH_4OH+NH_4F the crack is less than NH_4OH but the samples seems more foggy, in other words, less transparent. When using NH_4OH+NH_4F+DCCA as catalysis geometrical shape enhancement because of Drying Control Chemical Additives (DCCA) effected on microstructure.

Conclusion

The increase of contact angle and surface area affected by addition different catalysis, in the same time, the density effect on these additions. These chancing clear on FTIR blot , it's found that the addition of three catalysis enhance the transparency and the inner stricture but the density will became high and the hydrophobicity will decrease , the different catalysis effected on geometrical shape of silica aerogel, as we can dispose of cracks by using Drying Control Chemical Additives.

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