



# Effect of water content on properties of one-step catalyzed silica aerogels via ambient pressure drying



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## ABSTRACT

Tetraethylorthosilane was hydrolyzed and condensed in methanol as solvent, and catalytic aqueous ammonium fluoride and different amounts of water as co-solvent. The prepared gels were aged and solvent exchanged by *n*-hexane. The surfaces of the gels were modified using trimethylchlorosilane. Finally ambient pressure drying was performed. The surface area of the samples was determined by BET analysis and the pore size distributions were measured using the BJH method. FT-IR spectroscopy was used to confirm surface silylation. Compressive properties were investigated before drying. By increasing the amount of water, gelation time decreased significantly and compression modulus rose by increasing water content. Specific compression modulus (modulus/density) of the samples exhibited decrease with larger water content. The BET and BJH results showed that at first by adding more water, the specific surface area of silica aerogels decreased, this declination is more significant for the sample with 3 molar parts of water and after that, the surface area again increased slightly. The FE-SEM micrographs showed the pearl necklace structure for prepared samples.

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## 1. Introduction

Silica aerogels are low-density, high surface area, highly porous solids composed of approximately 90% of air [1–6] traditionally synthesized by the sol–gel polymerization of alkoxysilanes under the presence of an acid or base catalyst [3], and then supercritically dried in an organic solvent [3], liquid CO<sub>2</sub> [7–11] or via an ambient pressure drying (APD) route [12–16]. The supercritical drying method is costly and risky. In order to overcome these problems, the ambient pressure drying method has been developed by Prakash et al. [17] and has got more attention. Therefore in present studies we have adopted the commercially attractive ambient pressure drying method for drying of the gels.

Because of their unique properties, aerogels as core of numerous researches are functional in a variety of application fields such as thermal insulators, encapsulating agents, porous separation media, catalyst supports, adsorbents, particle capture agents, and ICF (Inertial Confinement Fusion) targets [3,6,18]. Recently hydrophobic granular silica aerogels have been successfully used for adsorbing phenol from water [19].

Although some researches have been done toward making aerogel from other metal oxides as precursor, silica aerogels have got huge attention in recent years; it could be due to wider application range for silica aerogels and also more available and economical precursors for these types of aerogels and also possibility of ambient pressure drying [4,20].

The primary stage in silica aerogel synthesis is carried out mainly through the hydrolysis and condensation of nano-sized colloidal silica particles produced by sol–gel processing in aqueous solutions containing alcohol, catalyst and silica precursor which could be sodium silicate (water glass) [21–26] or alkoxides like tetraethylorthosilane (TEOS) [11,13,16,27–30], tetramethylorthosilane (TMOS) [10,31] or methyltrimethoxysilane (MTMS) [32]. Although water glass is cheaper and more promising for commercial production of silica aerogel, it needs to be ion exchanged by cation exchange resins to remove Na<sup>+</sup> ions [25]. V. Rao et al. utilized water vapor passing over gels for removing of sodium ions and facilitation of applying sodium silicate precursors in commercial production of silica aerogels [21], huge consumption of expensive silylating agent for surface modification of the hydrogels produced from water-glass and more acquired solvent used for the water replacement in pores of water-glass based gels, makes this route quite expensive [13], so it could be told that production of sol–gel from tetraethylorthosilane (TEOS) is easier and has been extensively used as precursor, hence TEOS was also used in this study. There are two common routes in preparing gel from TEOS precursor: a) two-step synthesis of aerogel which includes preparing an acid catalyzed solution of TEOS and then obtaining sol–gel by adding basic catalyst to the TEOS solution [13]; and b) one-step sol–gel preparation by applying catalyst system [12]. Although ammonium hydroxide is the most common basic catalyst employed in the synthesis of alcogels, it causes long gelation time and increased bulk density of the silica aerogel. The reduction in gelation time and density of the aerogels is a considerable advantage for practical purposes. Fluoride catalysts (NaF, NH<sub>4</sub>F and HF) are known for their ability to boost gelation and reduce its time to minutes. Therefore,

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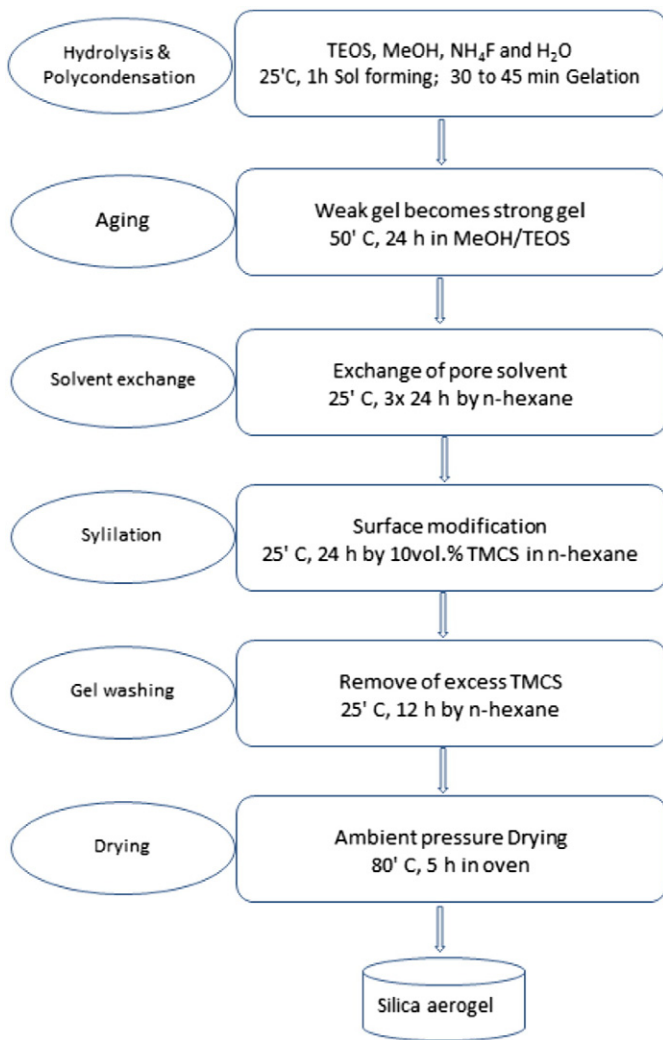


Fig. 1. General schematic of silica aerogel synthesis.

fluoride anion catalysts are of great interest, despite their strong toxicity, which obviously has to be taken into account in practical situations [33]. Therefore here like our previous work [12] we used a one-step synthesis method by applying aqueous  $\text{NH}_4\text{F}$  solution as catalyst which is simpler and more promising in the way of commercializing silica aerogel. Because supercritical drying is dangerous, time consuming and expensive, consequently new synthetic methods of aerogel have been attempted to overcome the disadvantages of supercritical drying by ambient pressure drying. In APD route after sol-gel preparation, aging at room temperature in order to strengthen the gel network structure and exchange of the pore fluids in wet gel with a volatile liquid such as ethanol or *n*-hexane takes place followed by surface modification [1,2,18].

Generally speaking in preparing silica aerogels by ambient pressure drying different parameters such as solvent type and its amount in hydrolyzing procedure, water content, pH of solvent, catalyst type and its amount, solvent type, temperature and time duration of aging, solvent exchange agent type, and temperature and condition of drying have significant effect on final properties of produced silica aerogel [1, 7–12]. In our previous paper, the role of solvent type, time and temperature of aging on properties of synthesized silica aerogels was investigated comprehensively. It is obvious that water has an essential role in the hydrolysis and condensation stage for obtaining sol-gel [33].

In our research low-density TEOS-based silica aerogels catalyzed by  $\text{NH}_4\text{F}$  were prepared with different amounts of water via the APD route

Table 1  
Gelation time of samples.

Water content (W/T) <sup>a</sup>	Gt (min)
1	40
1.5	36
2	33
3	28
5	22
7	18
9	17

<sup>a</sup> Molar ratio of water to TEOS.

and the effect of water content as one of the most important factors on gelation time, the surface area by Brunauer–Emmett–Teller (BET) and Barrette–Joyner–Halenda (BJH) methods, and the pore size structure and compressive properties of the samples were investigated. FT-IR spectroscopy was also used to confirm surface silylation.

## 2. Experimental

### 2.1. Materials

In this study TEOS (tetraethoxysilane, Fluka, Switzerland), methanol (Pure Methyl alcohol, Arak Petrochemical Co., Iran), *n*-hexane (Merck chemicals), 0.4 wt.% aqueous solution of  $\text{NH}_4\text{F}$  (ammonium fluoride, Sigma-Aldrich, Germany), and deionized water were used as received. Also 10 vol.% TMCS ( $\text{Si}(\text{CH}_3)_3\text{Cl}$ , 99% Sigma-Aldrich, Germany)/*n*-hexane solutions were prepared for surface modification of samples.

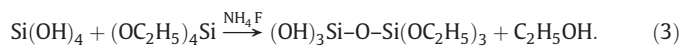
### 2.2. Sample preparation

In this study silica sol was prepared by ammonium fluoride catalyzed condensation. In the first step, TEOS, methanol,  $\text{NH}_4\text{F}$  and  $\text{H}_2\text{O}$  were combined in the molar ratio of  $1:8:2 \times 10^{-3}:\alpha$  ( $\alpha$  was 1, 1.5, 2, 3, 5, 7 or 9 by considering water content in aqueous catalyst solution as one molar part) respectively. Silica hydrogels were prepared by hydrolysis and poly-condensation of TEOS precursor according to following reactions [25]:

Hydrolysis:



Silica poly-condensation:



A sol was prepared by vigorous stirring of the mentioned materials. Then the obtained sols were cast into PE mold with 46 mm in diameter

Table 2  
Physical properties of samples.

Water content (W/T) <sup>a</sup>	Density ( $\text{g}/\text{cm}^3$ )	Porosity (%)	Surface area ( $\text{m}^2 \text{g}^{-1}$ )	Mean pore diameter (nm)	Total pore volume ( $\text{cm}^3 \text{g}^{-1}$ )
1	0.123	94.41	649	16.5	2.64
1.5	0.132	94.00	589	16.8	2.44
2	0.156	92.91	571	16.1	2.28
3	0.178	91.91	466	22.1	2.46
5	0.218	90.09	482	21.0	2.44
7	0.247	88.77	495	18.5	2.27
9	0.262	88.09	505	15.8	1.93

<sup>a</sup> Molar ratio of water to TEOS.

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