‘Seeded’ growth of silica aerogel by tetraethoxysilane and trimethylchlorosilane co-precursor method

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A B S T R A C T
Silica aerogels were successfully synthesized by tetraethoxysilane (TEOS) and trimethylchlorosilane (TMCS) co-precursor method. silica gels were prepared in two steps. For the introduction of the hydrophobic group –Si(CH3)3 and its presence at the growth front, the degrees of the condensation and the crosslinking of the samples should be affected. Depending on the NH4OH-catalyzed reactions at different temperatures in the second step, ‘seeded’ growth and direct growth with different mechanisms were observed and investigated. For the sample obtained from ‘seeded’ growth, first gelation results in the dense gel with good hydrophobic behavior, relative low specific surface area. After the second gelation, the final aerogel was found to have the increased specific surface area and the decrease in the hydrophobicity. The experimental results show little difference between the final aerogel product from seeded growth and the sample from direct growth, but different growth mechanisms were revealed.

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1. Introduction
Aerogels are porous inorganic polymers, which have high specific surface area, low density, low dielectric constant and low thermal conductivity [1,2]. These features of aerogels make them attract considerable attention for their new science and technological applications as catalysts [3], thermal insulators in aerospaces [4], and novel electrochemical device components [5]. A great deal of research has been conducted on traditional SiO2, Al2O3, and TiO2 aerogels [6,7]. In order to produce high-quality monolith aerogels, supercritical fluid drying has been adopted generally. In the preparation of aerogels, one of the key steps is the formation of the highly porous three-dimensional network. Network formation includes two important reactions: hydrolysis and condensation. A metal hydroxide (MOH) forms by hydrolysis –O–M) is obtained through condensation and aggregation. For the silica aerogel, the adsorption of water vapor does not harm its backbone, but contact with liquid water can lead to disastrous results in exposed environments. Recently, chemically modifying the surface of gel and ambient pressure drying methods are developed for the low cost and more safety [8,9]. Chemical surface modification converting the surface hydroxyl (–OH) groups to non-polar (–OR) groups can alter the ionic characteristics and surface free energy of the particles and the resulting gel, but multiple chemical treatments need long time and several washing and solvent exchange steps to get the hydrophobic silica aerogel in terms of low cost and safety. And co-precursor method [10–12] has been developed to protect the aerogel from damage by eliminating the attractive forces between water and the silica surface.

The silica sol has been used as a nanoscale glue to prepare composite gels upon gelation to form a range of chemically and physically diverse particles into the three-dimensional silica network [13]. Using this method, the nanoscale mesoporous composite with required optical, chemical, or electrical properties can be prepared by the introduction of the second solid phase to the gel network. Here, we investigate the preparation of silica aerogel by using tetraethoxysilane (TEOS) and trimethylchlorosilane (TMCS) as co-precursors. Depending on the reaction conditions, ‘seeded’ growth and direct growth phenomena are both observed. For the ‘seeded’ growth, silica gel can be incorporated into the uncondensed sol to form pure silica ‘composite’ and the growth mechanisms are discussed.

2. Experimental
2.1. Sample preparation
Tetraethoxysilane (TEOS) and trimethylchlorosilane (TMCS) were purchased from Sigma-Aldrich Chemical Co. Ethanol, HCl and NH4OH were purchased from Beijing Chemical Co. All the reagents were directly used without further dilution. Silica gels were prepared in two steps. Firstly co-precursors (TEOS and TMCS) were mixed with ethanol, substoichiometric amount of water and HCl solution (Molar ratio in the
solution; TEOS:TMCS:Ethanol:H2O:HCl = 1:0.9:3.1:1.2:7×10^{-4}). The mixture was refluxed at 70–80 °C for about 3–4 h to get pre-polymerized co-precursors. The solvent was removed by distillation. Finally the distilled solution was redissolved in ethanol and reacted with additional water/ethanol solution under NH4OH catalyzed conditions (ethanol:H2O:NH4OH = 1:7:5×10^{-4}) at room temperature (seeded growth) and 50 °C (direct growth). The process flowchart is shown in Fig. 1. The gels were washed by N-hexane and left to dry at 50 °C for 4 h at ambient pressure to get aerogel.

2.2. Characterization

The N2 adsorption–desorption isotherms were obtained by using Beishide Instrument-ST, 3H-2000PS2 equipment. The thermogravimetric analysis (TGA) was collected at the TGA/SDTA851e thermogravimetric analyzer from room temperature to 1000 °C. The measurement of infrared spectra was performed on a Nicolet Impact 410 FTIR spectrophotometer. The static contact angles of the samples were measured on the SL200B contact angle meter. 29Si NMR spectra were conducted on the Varian Infinity Plus 400 NMR spectrometer, fitting the samples in a 7 mm ZrO2 rotor. The microstructure of the aerogel was probed using a Scanning Electron Microscope (FEI-SEM, JHelios Nano Lab 600i).

3. Results and discussion

3.1. Seeded growth of silica gels

Fig. 2 shows the pictures and the schemes of the synthesis of silica gels from TEOS and TMCS co-precursor method. Let us look at the first route (from co-precursors to Sample A to Sample B). When the distilled solution was redissolved in ethanol and reacted with additional water/ethanol solution under NH4OH catalyzed conditions at room temperature, seeded growth of the silica gels occurs. Dense gels (as seed in the second gelation) were prepared by the first gelation. Then the dense gels were stirred strongly to get homogeneous colloidal solutions. Seeded growth was observed and final silica gels were synthesized by the second gelation. The dense gels and final silica gels were

![Flowchart with descriptions](image)

**Fig. 1.** Experimental procedure of the co-precursor method.

![Images and schemes](image)

**Fig. 2.** The optical images (i) and the schemes (ii) of the prepared wet gels.
dried at ambient pressure to get the aerogel products Sample A and Sample B, respectively.

The porosity was characterized by nitrogen sorption analysis in order to examine the surface properties of the aerogel porous structures.

The adsorption–desorption isotherms of the aerogel products Sample A and Sample B and their pore-size distributions obtained by BJH method are displayed in Fig. 3. According to the calculation, the specific surface area is 367 m²/g, and the pore volume and the pore size are 0.37 cm³/g.

**Fig. 3.** The N₂ adsorption–desorption isotherms for the aerogel products (a: Sample A; c: Sample B) and their pore-size distributions obtained by BJH method (b: Sample A; d: Sample B).

**Fig. 4.** SEM micrographs of the aerogel products Sample A and Sample B.
Water was placed on the sample surface to determine the wettability. The infrared spectra of the as-synthesized products Sample A and Sample B. The bands at 1080 and 450 cm$^{-1}$ are attributed to the presence of a Si–O–Si network. The FTIR results indicate the successful introduction of the hydrophobic and hydrophilic groups on the silica surface.

In order to further understand the seeded growth mechanism of the silica gels and the chemical environments of the Si atom, $^{29}$Si NMR measurements were conducted and the spectra are displayed in Fig. 8. The signals from $-80$ to $-120$ ppm are attributed to the presence of a silicon nucleus in a tetrahedral oxygen environment, conventionally indicated by the $q_n$ notation [14,15].

The formation of dense gels results from the first gelation of the pre-hydrolyzed co-precursors and its growth mechanism looks like the limited monomer cluster growth (RLMC). In this model, hydrolysis is the rate-determining step under basic conditions and reaction at the central silicon atoms of an oligomer unit is favored. The resulting network is characterized by colloidal gels [18,19]. For the faster condensation, hydrolyzed species are consumed immediately and the clusters grow mainly by condensation of monomers, because condensation of clusters with each other requires unfavorable inversion of configuration at one of the silicon atoms involved in the reaction [20].

The infrared spectra of the as-synthesized products Sample A and Sample B. The infrared spectra of the as-synthesized products Sample A and Sample B. The bands at 1080 and 450 cm$^{-1}$ are attributed to the presence of a Si–O–Si network. The FTIR results indicate the successful introduction of the hydrophobic and hydrophilic groups on the silica surface.

The hydrophobicity of the dried silica aerogel products can be verified by the static contact angle measurements directly. A droplet of water was placed on the sample surface to determine the wettability of Sample A and Sample B and the contact angles were obtained. The results are shown in Fig. 7. The contact angle of Sample A is $120^\circ$, which indicates its hydrophobic feature. For Sample B, the contact angle is $76^\circ$ which reveals the decrease in the hydrophobicity after second gelation. Compared with the strong hydrophilicity (contact angle $< 30^\circ$) of the sample prepared from single TEOS precursor method, the hydrophobicity of the silica aerogel products prepared by TEOS and TMCS co-precursor method was improved.

For the introduction of the hydrophobic group $\text{Si}(\text{CH}_3)_3$, its presence at the growth front, the degrees of the condensation and the crosslinking of the samples should be affected, which left the uncondensated sol after the formation of the dense gels with relative low specific surface area. And we observed the strong 15 ppm signal from the $\text{Si}(\text{CH}_3)_3$ groups on the silica surface and the similar intensity of $Q_3$-$\text{Si}$ and $Q_4$-$\text{Si}$ sites in Fig. 8 a). Then obvious hydrophobicity of Sample A was indicated in Fig. 7 a). When the dense gels with reactive $\text{OH}$ groups were stirred strongly to get homogeneous, seeded growth was observed and silica gels with high degree of crosslinking were synthesized. The decrease in the hydrophobicity after second gelation of Sample B was observed in Fig. 7 b), as indicated by the decrease in the intensity of $-\text{Si}-(\text{CH}_3)_3$ signal and the increases in the specific surface area.

3.2. Direct growth of silica gels

When the distilled solution was redissolved in ethanol and reacted with additional water/ethanol solution under NH$_4$OH catalyzed conditions at higher temperature (about 50 °C), direct growth (second route: from co-precursors to Sample C) of silica gels was observed. Although the hydrophobic group $\text{Si}(\text{CH}_3)_3$ was involved at the growth front, the higher temperature favors the inversion of configuration at one of the silicon atoms involved in the reaction, and the condensation of clusters with each other can occur. Then we get the silica aerogel products directly.

The $N_2$ adsorption–desorption isotherm and the pore-size distribution of the aerogel product Sample C were displayed in Fig. 9. The results show that the specific surface area is 663 m$^2$/g, and the pore volume and the pore size are 0.29 cm$^3$/g and 2.5 nm, respectively. Also the FTIR and $^{29}$Si NMR results shown in Fig. 10 confirm the introduction of the hydrophobic group $\text{Si}(\text{CH}_3)_3$ on the silica backbone. The experimental results don’t show obvious differences between the final aerogel products Sample B (from seeded growth) and Sample C (direct growth), but different growth mechanism was revealed.
4. Conclusion

Using tetraethoxysilane (TEOS) and trimethylchlorosilane (TMCS) as co-precursors, silica aerogel with the hydrophobic group – Si(CH₃)₃ on the backbone was synthesized. Depending on the experimental conditions, seeded growth and direct growth with different mechanisms were observed and the hydrophobicity of both silica aerogel products was improved. In the future, the optimism of the ratio between TEOS and TMCS should be undertaken in order to improve the hydrophobic feature of such silica aerogel. Hopefully the investigation of the fundamental chemical processes of the co-precursor method is helpful for the future design of the silica aerogel at the molecular level.

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References

Fig. 10. The infrared spectra (a) and $^{29}$Si NMR spectra (b) for the aerogel product Sample C.