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Additive-Assisted Synthesis of Silica Gel with Large Pores

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ABSTRACT

The study investigated and compared silica gel derived from acid-catalyzed hydrolysis and condensation reactions of tetraethyl orthosilicate (TEOS) in the absence and presence of additives—namely, chloroform, pentanol and hexane. Analysis using scanning electron microscopy (SEM) revealed that silica gel prepared without additive was dense and compact. The addition of chloroform strongly influenced the gelation process such that formation of a three-dimensional network was inhibited. Similar results were observed when pentanol was used. The addition of hexane had a negligible effect on the prepared silica gel. Importantly, the utilization of an equivolume mixture of pentanol and hexane produced silica gel containing micron-sized pores in the gel matrix. The results indicated that the inclusion of additives during the gel formation process exhibited different influences on the prepared silica gel depending on the nature and amount of the additives.

Keywords: additives, silica gel, pore, gelation, sol-gel

INTRODUCTION

Materials possessing specific and adjustable properties are very important and are often demanded for both research and industrial applications. Silica is one of the most widely studied materials in basic research laboratories and is used in various applications, such as separations, coatings and supports, because it is highly stable, non-toxic and biocompatible (Miyazaki *et al.*, 2005; Luckarift *et al.*, 2006; Mohammad and Bhawani, 2007; Martínez *et al.*, 2010; Jang *et al.*, 2011). The modification of the nano- or micro-structure of silica typically involves the utilization of structure-directing agents such as surfactants (Chan *et al.*, 2001; Vickery *et al.*, 2009). The obtained material frequently needs vigorous washing or calcinations to remove the remaining structure-directing agents prior to use, especially for biological applications. Therefore, silica synthesis using a surfactant-free method is an alternative route. In this regard, simple and volatile additives are better choices for materials synthesis since post-synthetic processes are not required. In the present study, the utilization of volatile additives in the synthesis of silica material was investigated to understand their influences on the gelation process and the mechanism of formation of large micron-sized pores. An Understanding of the mechanism of structural and morphological modification could be of great importance in processing silica material and of general interest in material preparation for bio-related fields such as immobilization, encapsulation and controlled release.

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MATERIALS AND METHODS

All chemicals were analytical reagent grade and were used without further purification. Tetraethyl orthosilicate 98% (TEOS, $C_8H_{20}O_4Si$), hydrochloric acid and pentanol were purchased from Arcos Organics (Geel, Belgium), Sigma-Aldrich (St. Louis, MO, USA) and Merck Schuchardt (Hohenbrunn,Germany), respectively, and chloroform and hexane were purchased from RCI Labscan (Mueng Samutsakorn, Thailand).

Typically, a pre-hydrolyzed tetraethyl orthosilicate (TEOS) mixture was prepared by addition of 1 mL of 1 mM hydrochloric acid to 1 mL of TEOS in a closed glass vial. The mixture was stirred at 1,400 rounds per minute for 6 hr until a clear solution was obtained. Subsequently, the desired volume of additive (100–400 µL) was added to the clear solution and then stirred for 18 hr. The additives used in this study were chloroform, pentanol, hexane and a 1:1 mixture of hexane and pentanol. The products were washed repeatedly with deionized water and air-dried at room temperature for 24 hr. Scanning electron microscopy (SEM) analysis was performed using a field emission scanning electron microscope (model JSM-6301F; JEOL; Tokyo, Japan) operating at accelerating voltages between 10.0 and 20.0 kV. Samples for SEM were cut into an appropriate size and attached on an aluminum stub using a carbon sticky pad and were then gold coated. Fourier transform infrared spectroscopy (FTIR) was performed using an FTIR spectrometer (System 2000; PerkinElmer; Waltham, MA, USA) equipped with spectrum analysis software. Samples for FTIR were prepared using the KBr disk method as follows. The sample was typically ground with infrared spectroscopy grade potassium bromide (KBr) using a mortar and pestle and hydraulically pressed to a 12 mm diameter disk. The FTIR spectra were recorded from 4,000 to 400 cm^{-1} at a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

The addition of hydrochloric acid with stirring to tetraethyl orthosilicate produced a transparent mixture within 6 hr (Figure 1). The mixture gradually became viscous and transformed to a translucent gel within 24 hr. Upon air drying, the gel turned white and opaque; its size reduced by approximately 50% due to the loss of water. Images from SEM (Figure 2a) indicated that the surface of the gel was rather smooth. At the microscopic level, the gel matrix appeared compact and comprised tiny particles with a mean size of 34 nm (SD = 3; Figure 2b). Analysis of the gel by FTIR (Figure 3) showed characteristic absorption bands at 1,080, 950, 790 and 460 cm^{-1}, corresponding to asymmetric

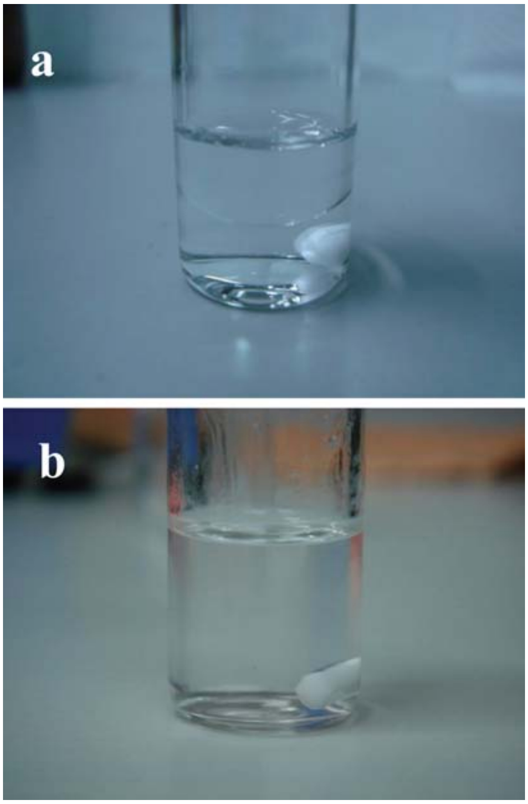

Figure 1 Images of the tetraethyl orthosilicate and acid mixtures: (a) after mixing showing two separate phases; (b) after 6 hr showing transparent single phase.

Si-O stretching, symmetric Si-O-Si stretching and Si-O-Si or O-Si-O bending modes of vibration of Si-O bonds, respectively (Brinker and Scherer, 1990; Olejniczak *et al*., 2005; Al-Oweini and Ei-Rassy, 2009). The broad band centered at about 3,500 cm^{-1} was attributed to O-H stretching of the silanol groups hydrogen-bonded to molecular water and O-H stretching of hydrogen-bonded water molecules (Al-Oweini and Ei-Rassy, 2009). The above results indicated that the synthesized sample was silica (SiO_2).

To study the influences of additives on the gel formation and morphology of the gel products, various amounts of liquid additives—namely, chloroform, hexane, pentanol and a mixture thereof, were added to the pre-hydrolyzed mixture. The addition of a small amount of chloroform negligibly affected the gel formation process. The pre-hydrolyzed mixture slowly turned into a solid gel. SEM results showed that the gel samples produced in the presence of 150-µL chloroform resembled those formed in the absence of additive. In contrast, a relatively large amount of chloroform (200 µL or more) strongly inhibited the gel formation such that no gel could be formed and only a viscous, white fluid was observed.

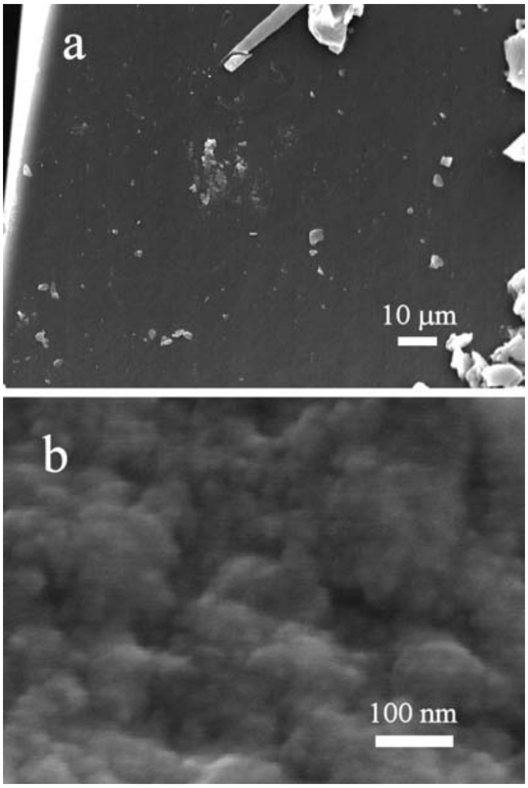

Figure 2 Scanning electron microscopy images of silica gel synthesized in the absence of additive: (a) at 10 µm scale; (b) at 100 nm scale.

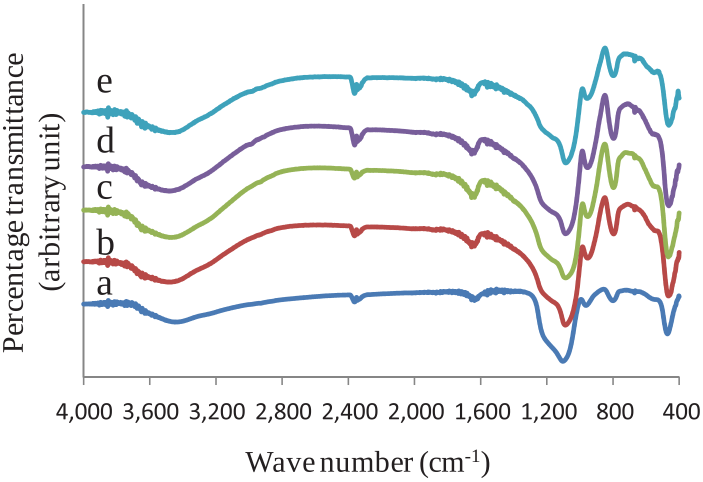

Figure 3 Fourier transform infrared spectroscopy spectra of samples synthesized with and without additives: (a) without additive; (b) with chloroform; (c) with hexane; (d) with pentanol; (e) with an equivolume mixture of hexane and pentanol.

The fluid turned to white powder after air drying. SEM images of the white powder showed lumps of particles with irregular shapes (Figure 4a). The addition of pentanol influenced the gel formation in a similar way as chloroform. The presence of a relatively large amount of pentanol (300 µL or more) retarded the gel formation and resulted in a viscous mixture, whereas the usage of a small amount of pentanol gave similar gels as those produced without additive. In both cases, FTIR spectra showed absorption bands consistent with Si-O vibrational modes of silica (Figure 3).

The addition of hexane had only a very small effect on the gel formation but interestingly induced the formation of voids in the gel matrix. SEM analysis of the products synthesized in the presence of hexane revealed a dense gel matrix with random micron-sized spherical pores on its exposed surfaces (Figures 4c and 4d). Translucent gels were produced in all cases, which were

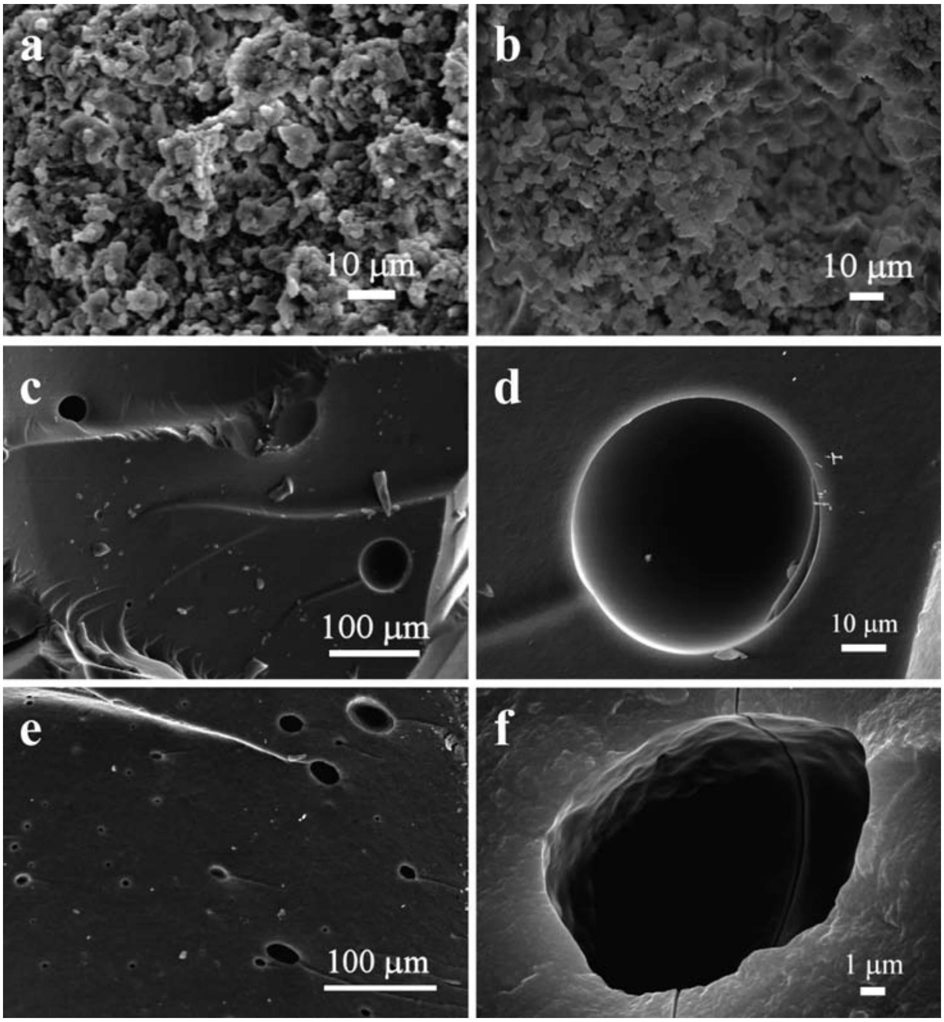

Figure 4 Scanning electron microscopy images of silica samples synthesized in the presence of: (a) 200 µL of chloroform; (b) 300 µL of pentanol; (c); (d) 200 µL of hexane, (e) 200 µL of 1:1 mixture of hexane and pentanol at 100 µm scale; (f) 200 µL of 1:1 mixture of hexane and pentanol at 1 µm scale.

independent of the amount of hexane used (100–400 µL). The contrasting results of the present case to the cases of using either chloroform or pentanol suggested that hexane played a significant role in inducing the pore formation. In addition, the SEM results showed that the pores were different in size and randomly dispersed in the gel matrix, suggesting that the droplets of hexane formed were polydisperse and non-uniformly distributed. Further syntheses using a mixture of hexane and pentanol were undertaken in order to understand the role of hexane in forming large micron-sized pores in the silica gel. SEM analysis of the samples produced in the presence of a 1:1 mixture of hexane and pentanol showed dense gel matrices with micron-sized pores. Since the pores were in the micron range, the measurement of pore size could be done using appropriate SEM image processing software. The number of pores was greater and the pore size distribution was narrower when compared with those produced in the presence of an equal volume of only hexane. The fact that using only pentanol failed to produce pores but its mixture with hexane considerably induced the pore formation suggested that hexane was an essential component in forming the pores. The presence of pentanol and hexane in this case appeared to synergistically promote the formation of stabilized droplets, leading to the formation of the pores. However, it was noteworthy that the gelation process was completely inhibited when the volume of pentanol used in the mixture was

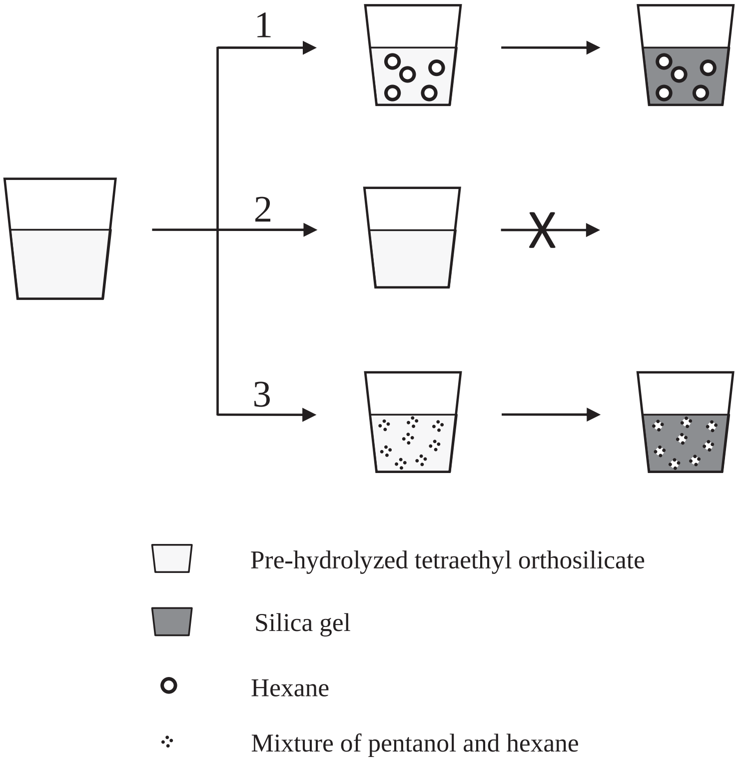

Figure 5 Schematic diagram showing the additive-induced formation of the pores in silica gel. 1 = Addition of hexane produced the oil droplets which finally remained as the spherical pores; 2 = Addition of chloroform or pentanol inhibited the gel formation; 3 = Addition of the mixture of hexane and pentanol yielded the fine droplets where pentanol molecules were mainly located at the interface and remained as the pores in the gel matrix.

300 µL or more. The FTIR spectra of the samples produced by using hexane and a mixture of hexane and pentanol showed absorption peaks consistent with SiO_2 vibrational modes (Figure 3).

A schematic diagram of pore formation in the gel matrix is proposed in Figure 5. Hexane was immiscible in the pre-hydrolyzed tetraethyl orthosilicate mixture; therefore, it formed spherical droplets and dispersed in the pre-hydrolyzed mixture. These droplets were stable during the gelation process and remained as spherical pores in the gel matrix. In contrast, chloroform and pentanol appeared to participate in and interfere with the gelation process such that no silica gel but only silica particles were formed. The above FTIR results confirmed the formation of Si-O-Si bonds, indicating that silicon alkoxide underwent normal hydrolysis and condensation reactions in all cases but the gelation process was interfered with only in some cases where either chloroform or pentanol was used. Importantly, the presence of pentanol with hexane promoted the production of more uniform pores in the gel matrix. Since pentanol contains hydrophilic and hydrophobic moieties in its structure, pentanol molecules presumably were located at the interface between the hexane droplet and the pre-hydrolyzed mixture and promoted the stabilization of the hexane droplets during the gelation process.

CONCLUSION

The influence of additives on the gelation process was investigated. It was found that polarity of the additives played important roles during the process. Chloroform and pentanol influenced the gelation process such that the process failed, whereas hexane did not participate in the gelation process. Interestingly, either hexane or its mixture with pentanol induced the formation of large pores in the final gel matrix. This fundamental knowledge could be beneficial for the introduction of large pores with adjustable sizes in silica materials and in other gel-like materials in general.

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