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INVITED PAPER: FUNDAMENTALS OF SOL-GEL AND HYBRID MATERIALS PROCESSING

Cosolvent-free synthesis of macroporous silica gels and monolithic silica glasses from tetraalkoxysilane–water binary systems: comparison between tetramethoxysilane and tetraethoxysilane

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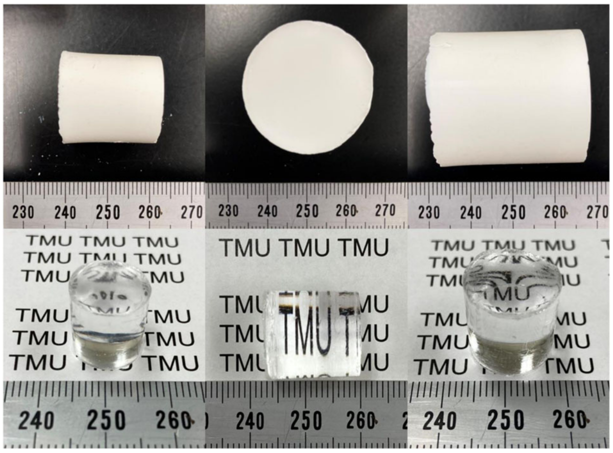
Abstract

Cosolvent-free (solventless) acid-catalyzed partial hydrolysis of tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS) followed by neutralization with imidazole ($pK_a = 7.0$) was employed to form macroporous silica gels via polycondensation-induced phase separation and concurrent gelation. The reactions of TEOS at 20 °C and subsequent drying in air yielded crack-free opaque macroporous xerogels. In contrast, cooling was necessary to derive opaque gels from TMOS, and the resulting xerogels obtained by reactions at 5 °C broke into pieces during drying due to the too small size of the pores. A macroporous silica xerogel prepared from 50 mmol (10.4 g) of TEOS was dried within 30 h in air, and subsequent sintering in a helium atmosphere at 1300 °C yielded a monolithic silica glass. The yield of silica glasses was higher than 99%.

Graphical Abstract

Photographs of two opaque macroporous xerogels prepared by cosolvent-free acid-catalyzed partial hydrolysis of TEOS followed by neutralization-induced gelation in parallel with phase separation, and silica glasses derived from these gels. The amount of TEOS used was 50 mmol for the gel and glass in the left column, and 100 mmol for those in the center and right columns.



Keywords Monolithic macroporous silica xerogel · Silica glass · Cosolvent-free sol–gel method · Neutralization-induced phase separation · Alkoxy group dependence

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Highlights

- Formation of monolithic macroporous silica gels was examined by a cosolvent-free (solventless) sol–gel method using tetraethoxysilane (TEOS) or tetramethoxysilane (TMOS) as silicon sources.
- Acid-catalyzed partial hydrolysis of TEOS and subsequent neutralization with imidazole ($pK_a = 7.0$) at 20 °C caused gelation accompanied by phase separation and formed opaque macroporous silica gels, which were easily dried in air without fracture and sintered into monolithic silica glasses with high yields exceeding 99%.
- Cooling was necessary to form opaque gels from TMOS, whereas the resulting xerogels were fractured because of the too small size of the pores.

1 Introduction

The sol–gel synthesis of silica glasses has been studied over several decades to form silica glasses at relatively low temperatures without melting [1–7]. However, the processing of monolithic gels and glasses is often difficult because of fracture during the drying of wet gels, originating from capillary force at air–liquid interfaces and the resulting uneven shrinkage [8]. This fracture problem can be avoided by supercritical drying [8, 9] or the incorporation of particulate silica fillers [10–12]. Other approaches include the reduction of capillary force by increasing pore size [3, 4, 13–16] and incorporating drying control chemical additives (e.g., formamide [17] and *N*,*N*-dimethylformamide [18, 19]) that reduce the surface tension of solvents. Capillary force in macropores is small and the drying of macroporous gels is relatively easy. Sol–gel processes accompanied by phase separation are useful in obtaining macroporous silica gels; when silica oligomers and solvent mixture are repulsive, the growth of silica oligomers and simultaneous decrease in mixing entropy lead to polycondensation-induced phase separation [20, 21]. Additives such as strong acids [22, 23], organic polymers [24, 25], and polar solvents (e.g., formamide [26]) have been used to promote phase separation. Similar phenomenon also occurs in acid-catalyzed mixtures of methyltrimethoxysilane and water because hydrophobic silica oligomers modified by nonhydrolyzable methyl groups are formed in hydrophilic mixture of water and methanol [27]. Silica monoliths have been prepared from mixtures of tetraalkoxysilane and water without using cosolvent (parent alcohol of the relevant tetraalkoxysilane), organic solvents, and other additives [28, 29], whereas the preparation of macroporous silica gels from such precursor solutions was unexplored.

Our aim was to form macroporous silica gels from mixtures of a tetraalkoxysilane and water without using other additives than acid and base catalysts. At pH $\simeq$ 7, hydrolysis is expected to be the slowest but polycondensation is fast [30]. The partial hydrolysis of a tetraalkoxysilane at small water to alkoxide molar ratios ($\lesssim$2) readily yields solutions containing silica oligomers with hydrophobic unreacted alkoxy groups [31]. When such a solution is mixed with water and quickly neutralized to suppress the hydrolysis of the residual alkoxy groups, hydrophobic silica oligomers may be precipitated from water-rich hydrophilic solvent mixture.

We found that this approach works well for preparing macroporous silica gels with tetraethoxysilane (TEOS) [32–34]. Its notable difference from conventional two-step acid-base hydrolysis [35, 36] is that solutions are neutralized not by a strong base like ammonia, but by a weak Brønsted base with $pK_a \simeq 7$, such as an acetate salt ($pK_a = 4.8$) [32, 33], imidazole ($pK_a = 7.0$) [34], and ethylenediamine ($pK_{a1} = 9.9$, $pK_{a2} = 7.1$) [34]. The resulting weak Brønsted base buffer stabilizes pH in the neutral pH range and improves the reproducibility of macroporous morphology. The macroporous silica gels prepared by this method have been utilized as the precursors of various types of rare-earth-doped silica glasses [37–39]. The resulting transparent glass-ceramics containing the nanocrystals of $(Gd,Pr)PO_4$ [40] and $(Tb,Ce)PO_4$ [41] exhibit bright ultraviolet and green photoluminescences, respectively, with internal quantum efficiencies close to unity. However, it is unclear if this strategy also operates in alkoxides other than TEOS.

The purpose of this study was to examine the cosolvent-free (solventless) synthesis of macroporous silica gels using two common tetraalkoxysilanes, TEOS and tetramethoxysilane (TMOS), and investigate the similarity and difference.

2 Experimental procedure

In this study imidazole [34] was selected as the base for neutralization. Dilute nitric acid was added to TMOS or TEOS at an alkoxide: H_2O:HNO_3 molar ratio of 1:x_1:0.002 (first mixing), and the mixture (solution 1) was stirred at 5 or 20 °C for 60 min in a sealed container to form a clear solution. An aqueous solution of imidazole prepared at an H_2O: imidazole molar ratio of x_2:0.005 (solution 2) was then added (second mixing). The imidazole to HNO_3 molar ratio in this study was set at 2.5, which was close to the typical base to acid molar ratio (2) to form a buffer solution. The resulting solution with an overall alkoxide: H_2O:HNO_3:imidazole molar ratio of 1:($x_1 + x_2$):0.002:0.005, where $x_1 + x_2$ was maintained at 10, was stirred for 1 min

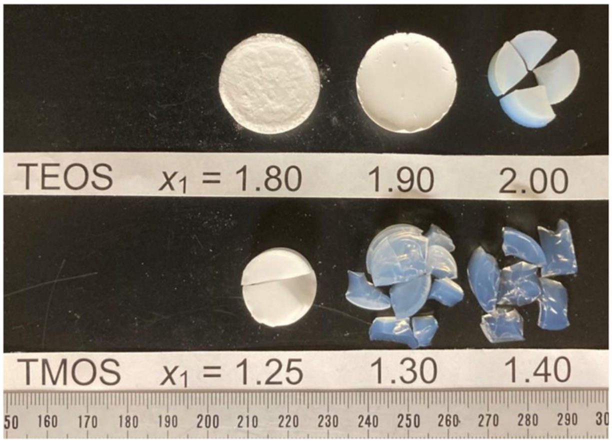

Fig. 1 Photograph of xerogels prepared from 25 mmol of TEOS at 20 °C (top) or TMOS at 5 °C (bottom), and dried at 60 °C

and then left to stand at the same temperature. Gelation time (t_g) was defined as the time from the second mixing until the loss of macroscopic fluidity. The beginning and ending times of phase separation (t_{psb} and t_{pse}, respectively) were similarly defined as the times of the appearance of turbidity and complete loss of transparency, respectively. Wet gels were aged at 60 °C for 24 h in sealed containers. After the disposal of the solvent phase, they were dried at 60 or 80 °C. The morphology of xerogels was observed by a scanning electron microscope (SEM, Phenom Pro, Thermo Fisher Scientific). Several xerogels were sintered in a tube furnace heated at a rate of 200 °C h^{-1} and maintained at the target temperature. The sintering atmosphere was changed from air to helium at ~600 °C.

3 Results

Solutions 1 became clear in ~40–50 min at 20 °C in the TEOS system and in ~1 min at 5 °C in the TMOS system. The TEOS-based gels were prepared at 20 °C. In contrast, the TMOS-based solutions were reacted at 5 °C because their gelation was very fast ($t_g < 1$ min) at 20 °C. After the second mixing, clear solutions were once obtained at $x_1 \geq 1.8$ in the TEOS system and $x_1 \geq 1.25$ in the TMOS system, whereas their fluidity and clarity were gradually lost by gelation and concurrent macroscopic phase separation.

Figure 1 shows photograph of xerogels prepared from 25 mmol of alkoxide and gently dried at 60 °C for ~5–6 days. Opaque xerogels were formed from TEOS at $x_1 = 1.80$ and 1.90, and from TMOS at $x_1 = 1.25$. Translucent xerogels were obtained at larger x_1. The size of xerogels decreased with an increase in x_1. All translucent gels were fractured during drying. Opaque xerogels prepared from TEOS were crack-free, whereas cracking occurred during aging in the opaque wet gel derived from TMOS.

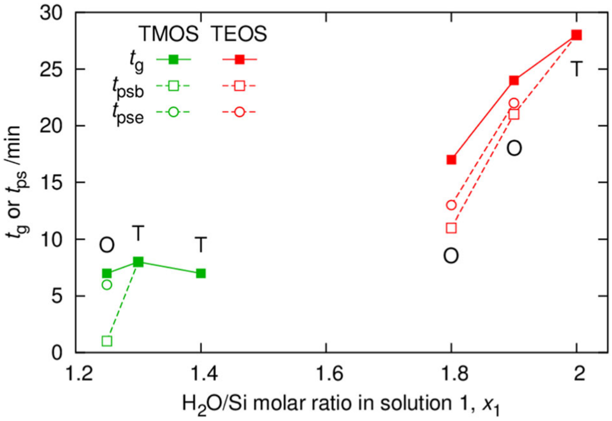

Fig. 2 Dependence on water to alkoxide molar ratio in solution 1 (x_1) of gelation time (t_g) and beginning and ending of phase separation times (t_{psb} and t_{pse}, respectively) of gels shown in Fig. 1, prepared from TMOS at 5 °C or TEOS at 20 °C. The symbols "O" and "T" denote "opaque gel" and "translucent gel", respectively

Figure 2 shows t_g, t_{psb}, and t_{pse} of gels shown in Fig. 1. Although reaction temperature of the TMOS system (5 °C) was lower than that of the TEOS system (20 °C), t_g was significantly shorter in the former than in the latter. In both systems, t_g of opaque gels was shorter than that of translucent gels, because phase separation concentrates silica oligomers in the silica-rich phase and enhances their polycondensation [20, 32, 33]. Gelation was preceded by phase separation ($t_{psb} < t_{pse} < t_g$) in opaque gels, and t_{pse} was absent in translucent gels because gelation halted domain growth before its completion. The appearance, gelation behavior, and their x_1 dependence of gels derived from TEOS agreed well with our previous reports [32–34]. The magnitude of the driving force for phase separation may be expressed by the normalized time required to complete phase separation, i.e., $(t_{pse} - t_{psb})/t_{pse}$. This value was much smaller in the TEOS system (~0.05–0.2) than in the TMOS system (~0.8), indicating that phase separation was more feasible in the TEOS system than in the TMOS system.

Figure 3 shows SEM images of xerogels shown in Fig. 1. Opaque xerogels prepared from TEOS at $x_1 = 1.80$ and 1.90 consisted of micrometer-sized spherical particles, whereas average particle size in the former gel was much larger than the latter. The structures of other gels were smaller than the resolution limit and unclear, even in the opaque gel prepared from TMOS at $x_1 = 1.25$.

Figure 4 shows photographs of a xerogel prepared from 50 mmol of TEOS at $x_1 = 1.96$ and silica glass obtained by sintering this gel at 1300 °C for 120 min. This xerogel was dried at 60 °C for 30 h, which was shorter than our previous report (2 days) [32]. Figure 4 also shows a xerogel prepared from 100 mmol of TEOS at $x_1 = 1.96$. This gel was dried at 80 °C for 4 days and converted to a monolithic silica glass by sintering at 1350 °C for 40 min. The weights of these

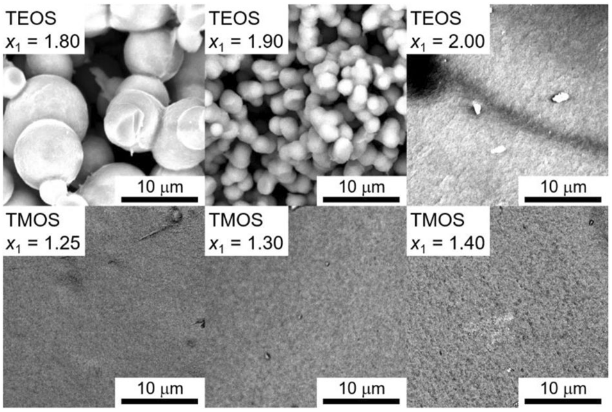

Fig. 3 SEM images of xerogels shown in Fig. 1

glasses prepared from 50 and 100 mmol of TEOS were ~2.979 and ~5.977 g, respectively, and their yields simply calculated from the weights and the molar mass of SiO_2 (60.084 g mol^{-1}) were ~99.2% and ~99.5%, respectively. SEM images shown in Fig. 4 were taken from a xerogel prepared from 25 mmol of TEOS at $x_1 = 1.96$.

4 Discussion

For each series of gels prepared from TMOS or TEOS, morphology was significantly different despite the same final solution compositions. In the TEOS system, the size of domains (spheres) varied by more than an order of magnitude with a small change in the water to alkoxide molar ratio of partial hydrolysis of solution 1 (x_1) from 1.8 to 2.0. This wide variation in domain size and its high sensitivity to preparation conditions are consistent with the characteristics of phase separation by spinodal decomposition.

Both TMOS and TEOS are immiscible with water, but become miscible upon hydrolysis. The hydrolysis of TMOS is faster than that of TEOS [42, 43]. Indeed, the homogenization of TMOS–water mixtures was much faster than that of TEOS–water mixtures. Thus, after the second mixing, residual methoxy groups in the TMOS system would be lost much faster than residual ethoxy groups in the TEOS system. Such gradual loss of residual alkoxy groups would make silica oligomers less hydrophobic in the TMOS system than in the TEOS system prepared at the same x_1. This hypothesis is supported by a large $(t_{pse} - t_{psb})/t_{pse}$ of ~0.8 in the TMOS system, suggesting a slow down of phase separation with time. The vulnerability of methoxy groups to hydrolysis makes phase separation in the TMOS system more difficult, and explains why small x_1 is necessary to prepare opaque gels in the TMOS system than in the TEOS system.

Opaque xerogels were larger than translucent xerogels (Fig. 1) because of small shrinkage (syneresis) during aging and low capillary force in large pores. Both the low capillary force and small shrinkage are favorable for reducing stresses during drying and suppressing fracture in opaque gels. However, the opaque gel prepared at $x_1 = 1.25$ from TMOS was cracked during aging. This crack formation is attributed to the small domain size and hence to the small pores of this gel, much smaller than that of opaque gels prepared from TEOS (Fig. 3). Other reasons include polycondensation after gelation, which would be more significant in the TMOS system, because methoxy groups are more reactive than ethoxy groups and the fraction of unreacted methoxy groups was larger than that of unreacted ethoxy groups in wet gels prepared in this study.

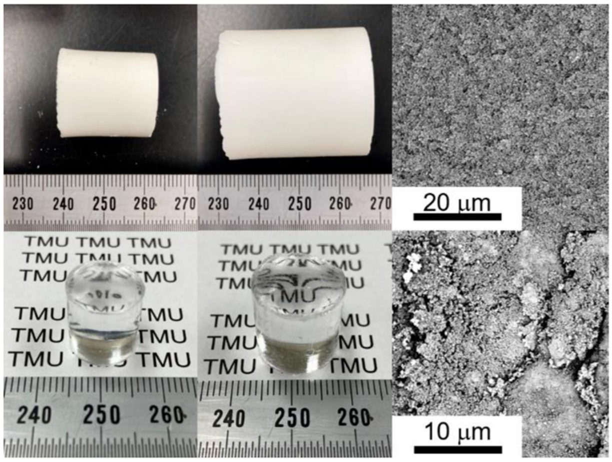

Fig. 4 Photograph of xerogels prepared at $x_1 = 1.96$ from 50 mmol (10.4 g) of TEOS and dried at 60 °C for 30 h (top left) and from 100 mmol (20.8 g) of TEOS and dried at 80 °C for 4 days (top center), and silica glasses obtained by sintering the former gel at 1300 °C for 120 min (bottom left) and the latter gel at 1350 °C for 40 min (bottom center) in a helium atmosphere. SEM images of a xerogel prepared from 25 mmol of TEOS at $x_1 = 1.96$ and dried at 60 °C are also shown with two different magnifications (right)

Under the conditions examined in this study, the preparation of crack-free macroporous gels from TEOS was easier than that from TMOS. We thus tried to reduce drying time by increasing drying rate. As shown in Fig. 4, a monolithic xerogel prepared from 50 mmol of TEOS was dried in 30 h at 60 °C, shorter than the time (2 days) recorded in our previous report [32]. A xerogel prepared from 100 mmol of TEOS was dried in 4 days at 80 °C. Simple solution composition (TEOS, water, and catalysts), relatively short processing time, and high silica yield ($\gtrsim$99 %) make this method attractive for the sol–gel synthesis of silica glasses.

5 Conclusions

Monolithic silica gels suitable as the precursor of silica glasses were prepared by acid-catalyzed partial hydrolysis of TEOS or TMOS and subsequent neutralization with imidazole (p$K_a = 7.0$). Solutions prepared from TEOS underwent gelation accompanied by polycondensation-induced phase separation at 20 °C, and formed opaque macroporous silica gels. Such gels were easily dried in air without fracture in several days and converted to monolithic silica glasses in high yields exceeding 99% by sintering in a helium atmosphere. Solutions prepared from TMOS also generated opaque gels by the same mechanism. However, cooling to slow down reactions was necessary, and crack-free xerogels could not be obtained because of the absence of macropores.

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Compliance with ethical standards

Conflict of interest The authors declare no competing interests.

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