JOURNAL OF MATERIALS SCIENCE 27 (1992) 520–526

Effect of ageing media on gel structure and monolithicity

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Silica gels were prepared from direct reaction of tetraethyloxysilane (TEOS) with water under acidic conditions. Different molar ratios of water to TEOS, and various ageing media were investigated to improve monolithicity. The transformation of the gel as a function of temperature was monitored by Fourier transform–infrared spectroscopy. The gel properties influenced by different ageing media were determined by measurement of density and specific surface area. The results show that by ageing wet gel in different solutions, the microstructure of a gel is changed, and also the monolithicity of the dried gel is improved.

1. Introduction

Preparation of silica glass from metal–organic compounds through the sol–gel process has received much attention, because this process has advantages that make it possible to synthesize shaped glass and glass-ceramics at relatively low temperature compared with the conventional melting method [1, 2]. Although the sol–gel method is very attractive, many problems still exist, as pointed out by Zarzycki [3]. Of these problems, the most serious one is thought to be the occurrence of cracks during drying of monolithic gel. In order to achieve monolithic gels, a hypercritical drying procedure [4] and use of chemical additives called the DCCA [5, 6] have been suggested. However, both methods have different limitations in routine glass production [7]. The nature of a sol and the resultant gel is determined by process factors among which the nature of the solvent is of importance. It is already known that the gel structure is changed by DCCA added to a sol during mixing and aged in the mother liquid. However, little attention has been paid to modification of wets gel and the structure, by ageing the gel in different polar solvents (secondary media) before subsequent treatments [8, 9]. This paper presents the effects of ageing media on properties of silica gel on the monolithicity.

2. Experimental procedure

2.1. Preparation of silica gels

It has long been known that the typical alkoxide route to silica sols comprises the catalysed reaction of TEOS and water in a mutual solvent to form a homogeneous sol. Mutual solvent is necessary because of the immiscibility between TEOS and water. However, solventless direct reaction of water with tetramethyloxysilane (TMOS) [10] and TEOS [11] have been reported. In this study no co-solvent was added. The starting materials used were tetraethyloxysilane (TEOS), nitric acid and distilled water. Solutions of ethyl alcohol (EtOH), propylene glycol (PG), both diluted in water, *N*,*N*-dimethyl formamide (DMF), TEOS, both diluted in EtOH, and acidic/basic water, the pH adjusted by HNO_3 and NH_4OH, were used as the ageing media.

The preparation of bulk gel is illustrated in Fig. 1. The alkoxide solution having the molar ratio of $TEOS:H_2O:HNO_3 = 1:x:0.025$ ($x = 3, 6, 10$) were prepared by mixing TEOS with the acidified distilled water at room temperature. The hydrolysis was completed in a few minutes, and a clear sol was formed. The sol was then cast into a plastic mould. Ageing of wet gels in various solutions was conducted after sols were gelled, shrunk by gelation and separated from the mould in a day. The aged wet gels were then dried in an oven at 60 °C by covering with a plastic film with a few pinholes to control the evaporation rate. In the adopted nomenclature, R is the molar ratio of number of water to number of TEOS.

2.2. Characterization methods

The dry gels were characterized by their bulk density and gel structure. To determine the bulk density and volume shrinkage, the diameter, length and weight of the dried gel bodies in cylindrical shape were measured using a vernier caliper and a balance.

Structural evolution of the gels as function of temperature was monitored by infrared transmission using a Fourier transform infrared spectrophotometer (FT–IR: Perkin-Elmer Model 1600). Gel samples were heat treated at the desired temperature in air at a rate of 0.75 °C min^{-1}. The samples were taken out of the furnace and allowed to cool in a desiccator, and then crushed into aggregates for the BET surface area determination.

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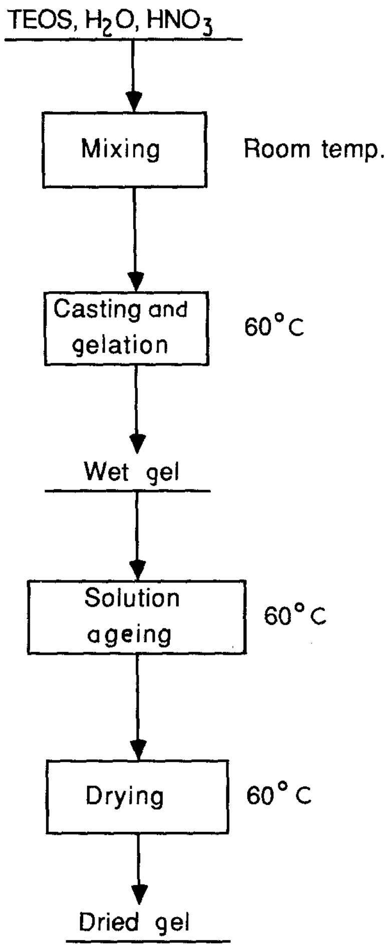

Figure 1 Schematic representation of the sol–gel process.

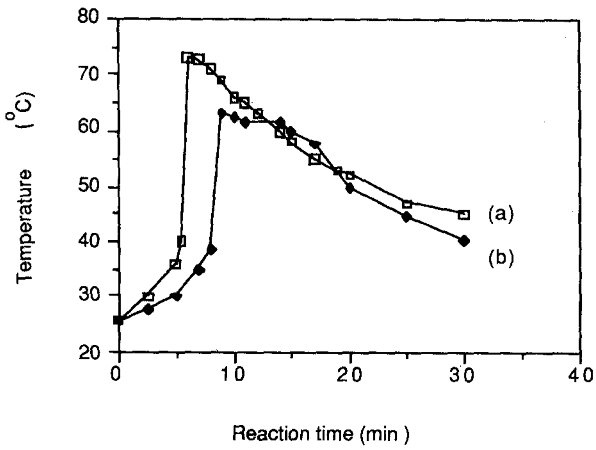

Figure 2 Effect of molar ratio of H_2O/TEOS on hydrolysis reaction. (a) $R = 3$, (b) $R = 6$ at room temperature.

The pore structure was determined by measuring its specific surface area and the pore volume by BET method using Quantachrome's Quantasorb. The pore volume was calculated from the specific surface area by assuming the pores to be cylindrical in shape. The gel samples were vacuum-dried at 150 °C overnight, and then degassed by heating at 125 °C for 20 min under a nitrogen flow for the nitrogen adsorption.

The surface of the dried gel, after vacuum-drying at 125 °C overnight, was observed by scanning electron microscopy (SEM). The specimen was then mounted on a stub and coated in vacuum with gold.

3. Results and discussion

3.1. Hydrolysis reaction

The temperature–time profile in Fig. 2 shows the effect of the water content on a reaction at a constant molar ratio of acid to TEOS of 0.025. An exothermic reaction is indicated in this acid-catalysed mixture. This should be owing to the exothermic hydrolysis reaction. The mixture transformed from two-phase dispersion to a clear solution within 6 min for $R = 3$ and 9 min for $R = 6$, reaching a maximum temperature of 74 and 64 °C, respectively; thereafter, the system cooled down. This should be the endothermic condensation reaction which takes place after hydroxyl groups on silicon have increased. The higher TEOS concentration ($R = 3$) accelerating the reaction rate is also evident (Fig. 2a). Although no solvent is used in the preparation of the sol, ethanol is released by hydrolysis of TEOS. The released alcohol caused the boundary between the phases to become more diffuse and to allow for an even higher concentration of alkoxy–silane molecules to react [10].

3.2. Formation of dried gels

Table I presents the monolithicity of the dried gels for $R = 10$ after drying at 60 °C. It shows that gels ageing in such media as acidic or basic water, water itself and diluted ethyl alcohol with water have a higher monolithicity than the unaged ones. It is noted that the gels tend to shrink more with increasing amount of water in ethyl alcohol, while using undiluted EtOH causes the gel to break due to the build-up of differential stress by quick evaporation of EtOH during drying. In addition, the monolithic gel is easier to obtain for solutions with a higher water content. However, a monolithic gel is difficult to yield for $R = 3$ unless the wet gel is aged with a basic solution (pH = 10).

3.3. Density and volume shrinkage of dried gels

The effect of ageing medium on the bulk density and the volume shrinkage of the dried gels is also reported in Table I. The bulk density of the dried gels ranges from 1.31–1.50 $g\,cm^{-3}$ for $R = 10$ and from 1.34–1.6 $g\,cm^{-3}$ for $R = 6$. The volume shrinkage ranges from 84–88 vol % for $R = 10$, and 81–86 vol % for $R = 6$. This indicates that the higher the water content, the less the bulk density, and the larger the volume shrinkage of the dried gel. The results are in agreement with Murtagh *et al.* [12]. The less shrinkage with decreasing R is due to the retention of more OH and OR groups. The difference in bulk density, therefore, can be attributed to the difference in the volume shrinkage. The gels aged in organic solution have less shrinkage than those aged in aqueous solution. This is due to the steric hindrance effect of the adsorbed molecules that remain in the gel after drying and prevent some hydroxyl groups from reacting together [5, 11] as well as the reduction in surface tension. This effect is supported by the observation

TABLE I Bulk density, volume shrinkage and specific surface area values of the dried gels at 60 °C after ageing for 1 day in various media

Solution	$R = 10$			$R = 6$		
	No. monolithic gel[a]	Bulk density[b] (g cm^{-3})	Vol. shrinkage (%)	Bulk density[b] (g cm^{-3})	Vol. shrinkage (%)	Surface[a] area (m^2 g^{-1})
Unaged	3	1.35	87.78	1.40	84.26	389
H_2O	5	1.32	87.62	1.34	84.91	384
EtOH[d]	4	1.34	87.88	1.36	85.69	368
DMF[e]	3	1.46	85.73	1.50	82.08	385
PG[d]	2	1.33	85.82	1.35	80.92	463
TEOS[e]	4	1.41	85.97	–	–	453
pH 2[f]	4	1.26	87.23	1.27	83.38	456
pH 4[f]	4	1.27	87.46	1.34	85.39	362
pH 8[f]	3	1.30	87.92	1.32	85.23	357
pH 10[f]	4	1.30	87.75	1.29	84.97	366

[a] No. monolithic gel is the number of monolithic gels produced in six samples.

[b] Bulk density values were averages of measurements on three samples for $R = 10$, and two samples for $R = 6$.

[c] Surface area values were averages of three measurements per sample.

[d] PG and EtOH were diluted in water to 33.33 vol %.

[e] DMF and TEOS were diluted in EtOH to 33.33 vol %.

[f] pH was adjusted using HNO_3 and NH_4OH.

that the gel shrinks less as the amount of organic solution increases. Lou and Tian [11] attributed the effect of the glycol on the structural property to the increase in Si–O–Si bond angle in the gel. It was considered that glycol as a bifunctional group might coordinate on the two adjacent silicons of the polymer chain, and induce the Si–O–Si to form a large angle.

3.4. Specific surface area and pore volume

In Table I the mean values of specific surface area of various solution-aged samples of $R = 10$ are given. The specific surface area of the dried gels changes with treatment in various ageing media. Fig. 3 illustrates that the specific surface area drastically decreases as the pH of ageing media increases to 4. In comparison with unaged gel, the pH 2 aged gel has a higher specific surface area than the unaged one. However, those samples aged in pH higher than 2 have a lower specific surface area. This corresponds to the acid-catalysed gel having a higher specific surface area than the base-catalysed one [13]. This finding provides an alternative to the base-catalysis process. The surface area can be tailored by the pH of the ageing solution. The variation of specific surface area with the composition of the solvent of DMF/EtOH and EtOH/H_2O is shown in Fig. 4. It indicates that the gel aged in DMF has a larger surface area than the gel aged in EtOH for $R = 6$. This figure does not exhibit an obvious relationship between the specific surface area and the composition of ageing media used. A similar kind of result was also reported for formamide additive [5].

Figs 5 and 6 illustrate the temperature dependence on the specific surface area of samples aged in EtOH and PG. A decreased specific surface area and total pore volume with an increased temperature are appreciated in the sample with EtOH ageing (Fig. 5). It shows that the consolidation does not begin until about 600 °C. However, the high values of the specific surface area measured suggest that the pore structure remains unchanged to temperatures in excess of 800 °C for the PG-aged gels (Fig. 6). This may be caused by the desorption of the adsorbed molecules on the gel surface affecting the densification process.

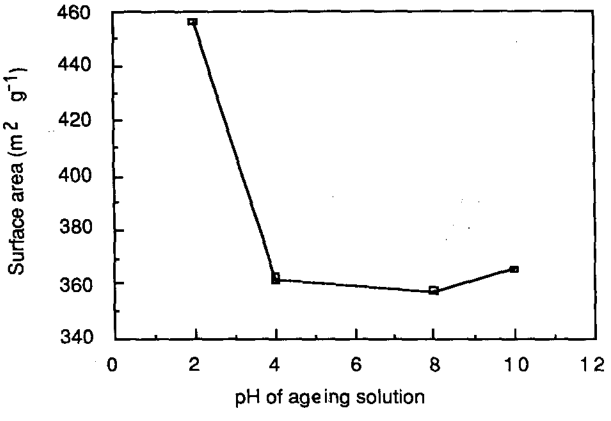

Figure 3 Variation of specific surface area with the pH of the ageing solution for $R = 6$.

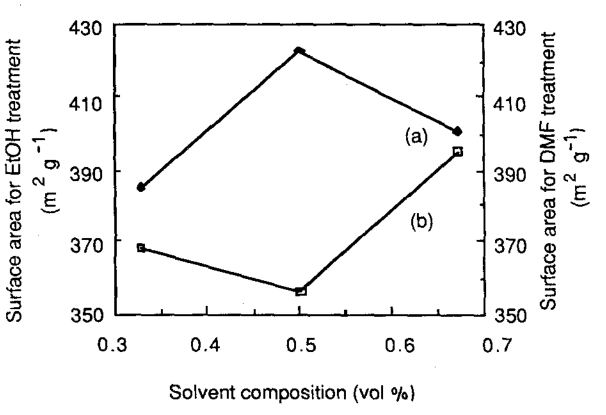

Figure 4 Variation of specific surface area with solution composition of (a) DMF in EtOH, (b) EtOH in H_2O for $R = 6$.

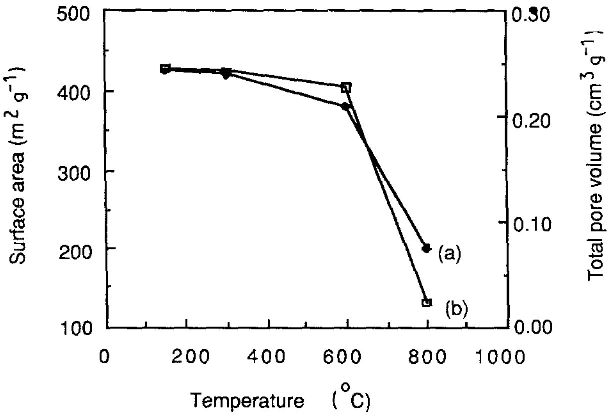

Figure 5 Variation of (a) total pore volume and (b) specific surface area with temperature for $EtOH/H_2O$-aged sample of $R = 10$.

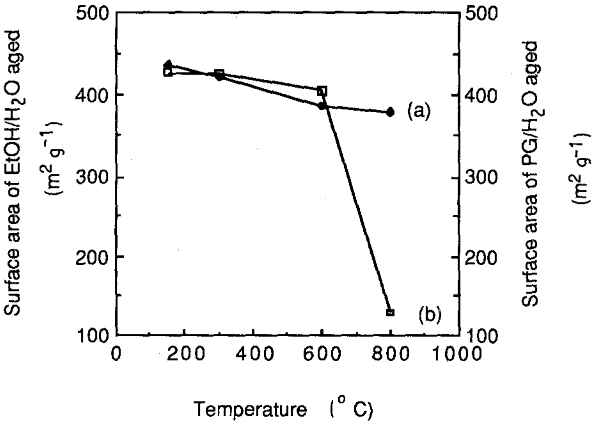

Figure 6 Variation of specific surface area with temperature, aged in different media: (a) PG/H_2O, (b) $EtOH/H_2O$ for $R = 10$.

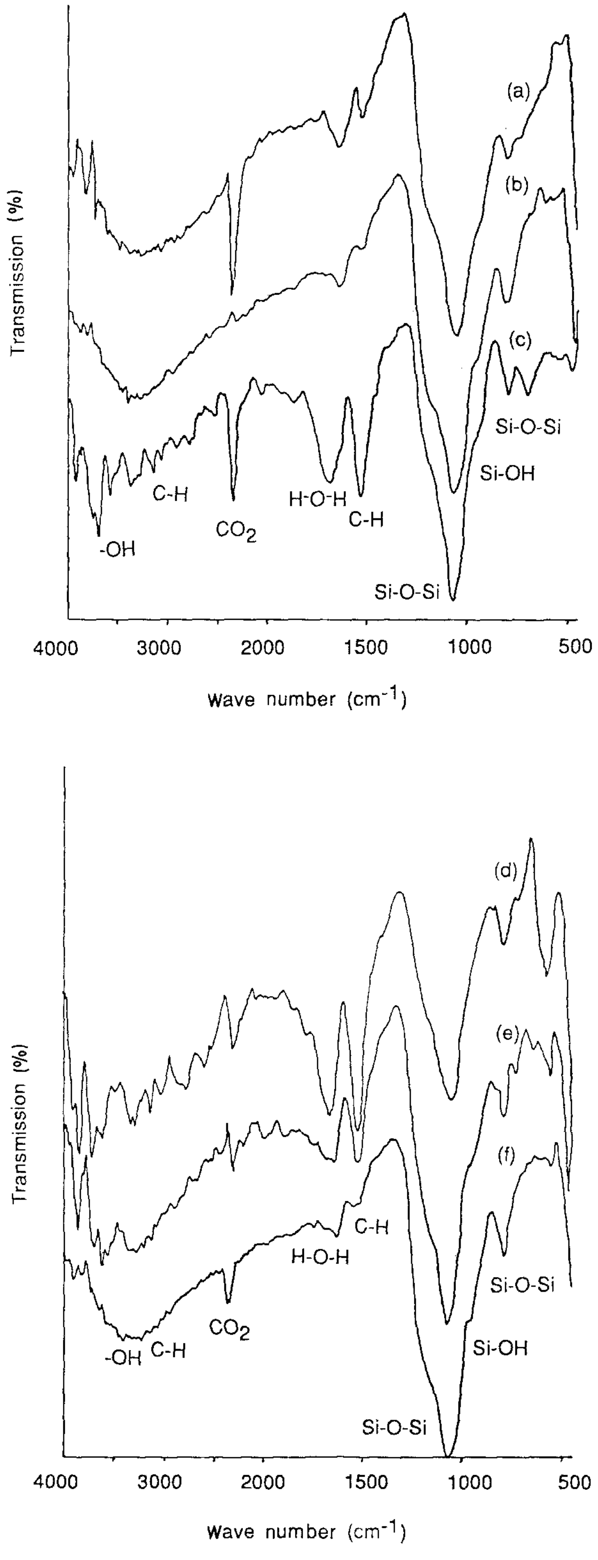

Figure 7 FT–IR spectra of silica gels for $R = 3$ with various ageing media: (a) DMF, (b) PG, (c) TEOS, (d) basic water (pH = 10), (e) water, (f) EtOH.

3.5. FT–IR transmission spectra

The FT–IR spectra from the gel for $R = 3$ aged in various media after firing at 600 °C are shown in Fig. 7. No great qualitative difference is observed. However, the increased intensities of the infrared bands at 1620 and 1500 cm^{-1} are observed in the cases of ageing in TEOS and in basic water. These peaks are assigned to H_2O and C–H, respectively. The increase of the peak intensities may be due to more adsorbed or trapped unhydrolysed TEOS and hence the need for more water to hydrolyse it in the gel as aged in the above media. With thermal treatment in air the structure of the gel changes. Fig. 8 shows the infrared spectra of gels for $R = 3$ aged in DMF as function of temperature. The bands at 3450 and 1620 cm^{-1} are, respectively, attributed to the stretching and deformation modes of hydroxyl groups and molecular water [14, 15]. The band at 1620 cm^{-1} tends to weaken upon heat treatment. The bands at 2800 and 1500 cm^{-1} can be associated with organic groups and imply an incomplete hydrolysis process [15]. This band also decreases on heating. The bands at 1220 and 1050 cm^{-1} are attributed to LO (longitudinal) and TO (transverse) Si–O–Si asymmetric stretching modes, respectively. The 800 cm^{-1} band is assigned to symmetric Si–O–Si stretching or vibrational mode of ring structure. In addition, the band at 950 cm^{-1} is assigned to the stretching mode of the Si–OH group [16, 17]. The reduction of intensity of this band is correlated with continued condensation with increasing temperature. Fig. 9 shows the effect of molar ratio of water to TEOS on a gel structure. The appearance of a broad band at 3150 cm^{-1} indicates the increase in the water content. In addition, the band at 1500 cm^{-1} decreases with an increase in R value as a result of the increasing overall hydrolysis, and consequent removal of organic group. The gel of $R = 6$ shows relatively

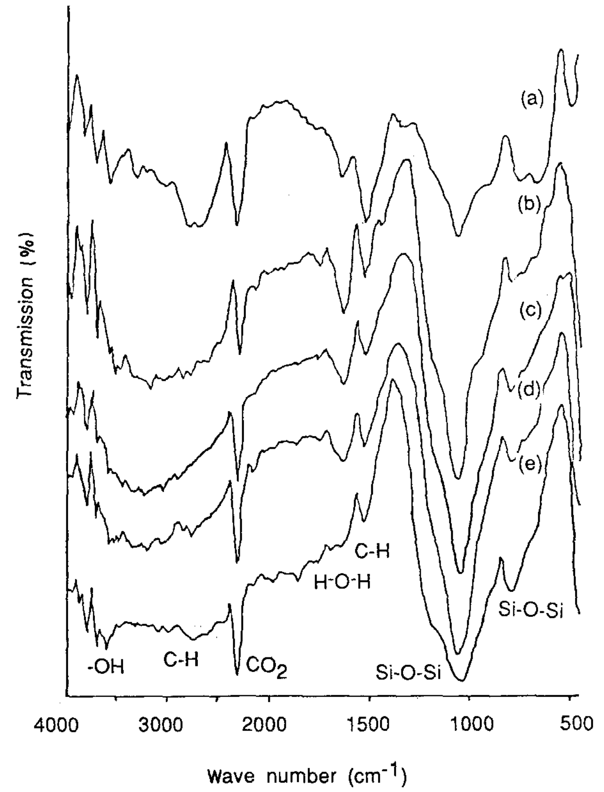

Figure 8 FT–IR spectra of silica gels for $R = 3$ with DMF ageing as a function of temperature: (a) 100 °C, (b) 300 °C, (c) 600 °C, (d) 800 °C, (e) 1000 °C.

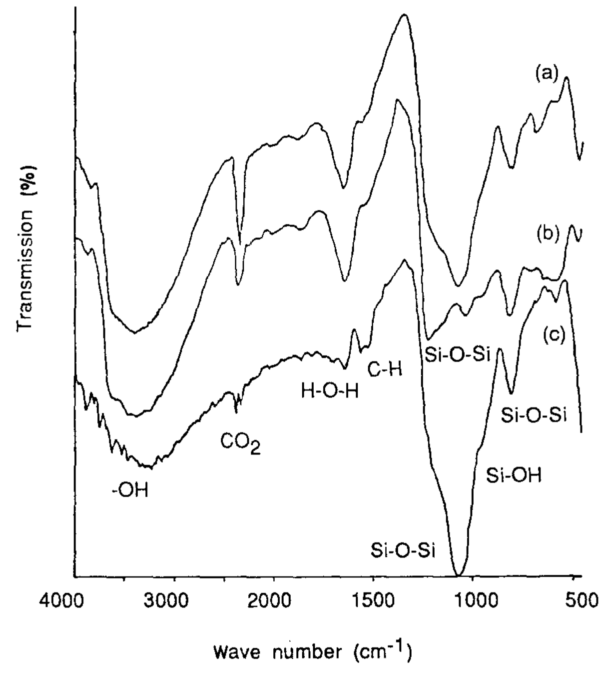

Figure 9 FT–IR spectra of silica gels as a function of molar ratio of H_2O/TEOS: (a) $R = 3$, (b) $R = 6$, (c) $R = 10$, heat-treated at 600 °C.

higher LO stretching mode than TO mode; it reverses in others.

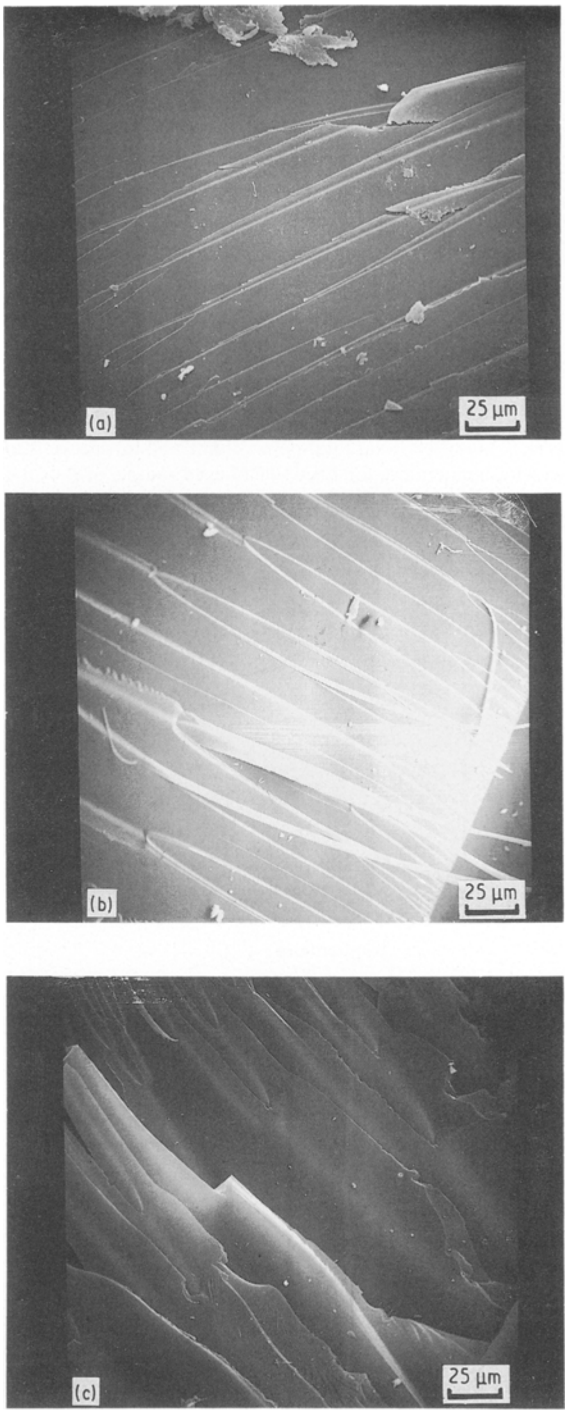

Figure 10 Scanning electron micrographs of the fractured surface of a silica gel dried at 110 °C with different water contents: (a) $R = 3$, (b) $R = 6$, (c) $R = 10$.

3.6. Gel microstructure

A set of micrographs for fractured surface of the dried gel at 110 °C is given in Fig. 10. These illustrate the effect of the water content for hydrolysis of TEOS on the gel structure. The gel prepared with a low water content ($R = 3$) shows a fibrous fracture pattern. This is due to the incomplete hydrolysis that causes gelation through linear chain formation. For intermediate water content ($R = 6$) a fibrous structure still appears. However, the gel prepared with a high water content ($R = 10$) shows a layer structure that indicates a high network formation. Similar results for $R = 1$ and 20 have been reported by Duran *et al.* [18].

Fig. 11 shows the different granular microstructures of the dried gels in different ageing media for $R = 3$. Both unaged and water-aged gels feature particles packed closely and interconnecting together between

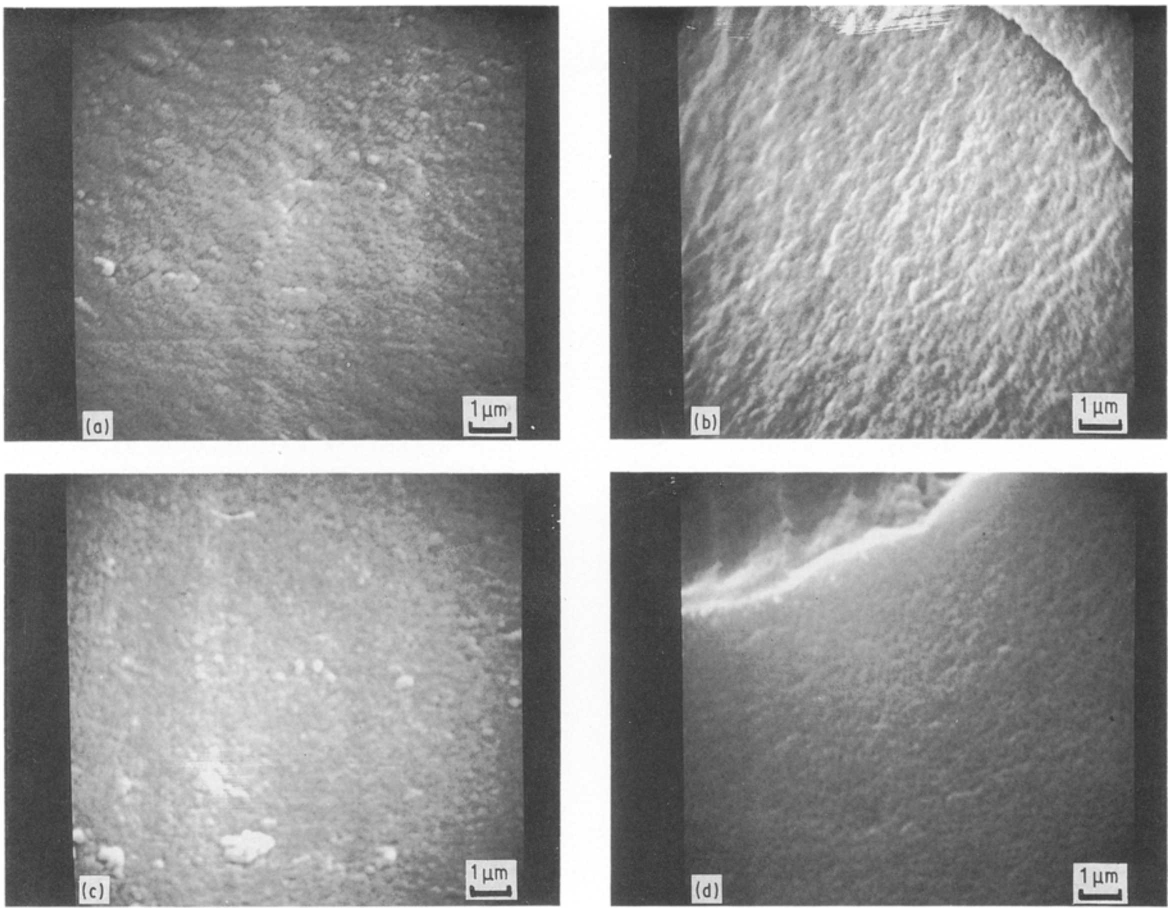

Figure 11 Scanning electron micrographs of a silica gel dried at 110 °C for $R = 3$, (a) without ageing treatment, (b) aged in H_2O, (c) aged in EtOH, (d) aged in PG.

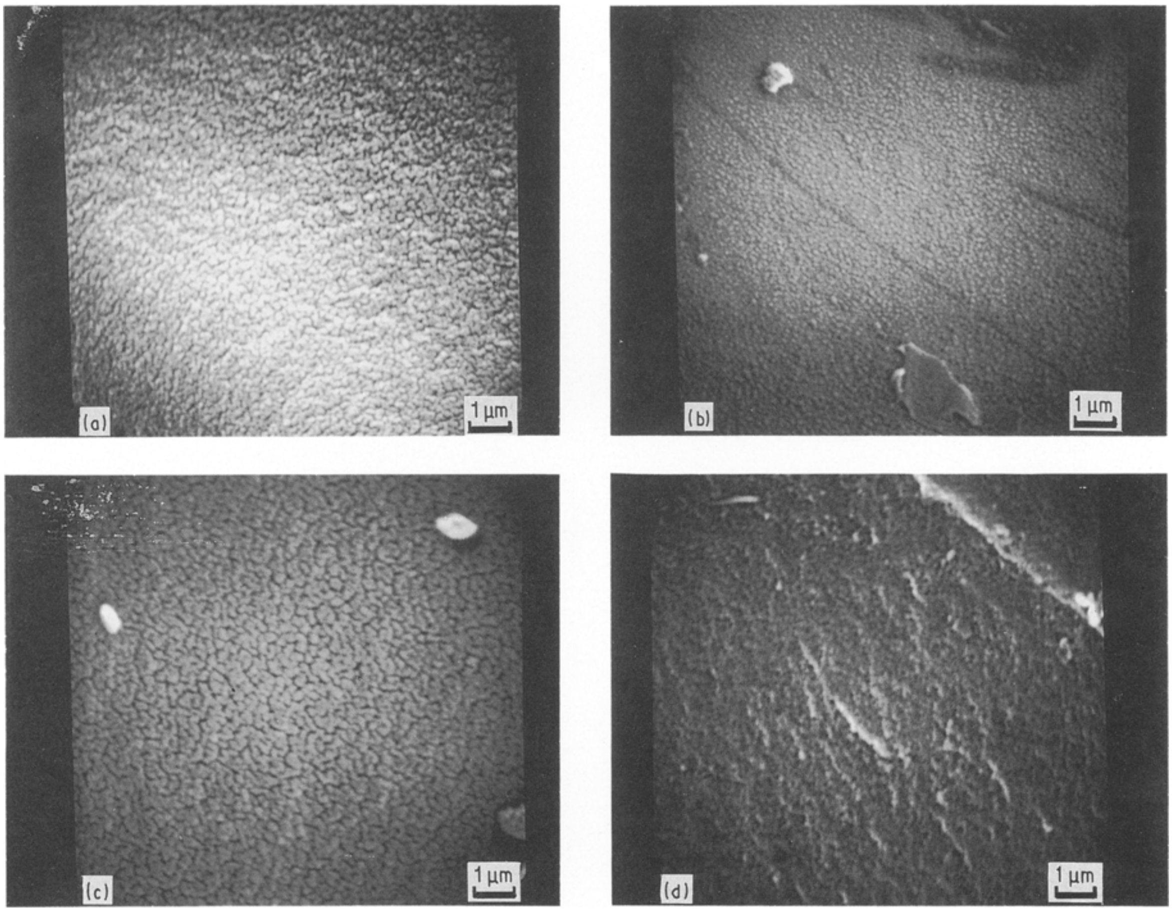

Figure 12 Scanning electron micrographs of a silica gel for $R = 3$, heat-treated at (a) 300 °C, (b) 600 °C, aged in water pH = 10, (c) 300 °C, (d) 600 °C, aged in water pH = 3.

particles. However, this feature disappears when the gel is aged in other media. In the case of ETOH-aged gel, a more particulate texture is observed, in which the particles are packed loosely and relatively large pores exist between the solid network. The pores are more evenly distributed throughout the gels on ageing in TEOS and PG. In the latter case, it seems that the gel is covered with PG molecules. The development of microstructure with heat treatment is shown in Fig. 12. The basic water-aged gel exhibits more homogeneous and particulate microstructure (a and b) than the acidic water-aged gel in which the interchain or interparticle bonding is formed after heat treatment to 600 °C.

4. Conclusions

1. The microstructure of a silica gel can be modified by ageing it in a secondary solution medium.
2. The solution ageing treatment of the wet gel improves the monolithicity of the dried gel.

Acknowledgement

The authors thank the State of South Carolina for financial support of this work.

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Received 28 September 1990
and accepted 18 March 1991