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Chemical effects of DCCA to the sol–gel reaction process

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The effects of drying control chemical additives (DCCA) on the growth of silica particles, gelation time and physical properties of the dry gel were examined in a two-step silica sol–gel process. *N,N*-dimethylformamide, *N,N*-dimethylacetamide and ethylene glycol (EG) were applied as DCCAs. The shapes of growing silica particles were distorted spheres on addition of DCCA. EG accelerated the gelation process. Despite the use of DCCA, crack-free, dry gels were obtained only under limited conditions.

1. Introduction

It is difficult to obtain a large amorphous silica monolith by directly drying a wet silica gel which is made through a sol–gel process due to intensive cracking during drying. The origin of the cracking has been attributed to capillary pressure generated in micropores in the gel during the drying process [1].

The magnitude of the capillary pressure can be expressed by the following equation [2]:

$$\Delta P = 2\gamma \cos\theta / r \qquad (1)$$

where γ is the surface tension of the solvent, r the capillary radius and θ the contact angle. This equation shows that ΔP can be decreased by decreasing the surface tension of the solvent and/or by increasing the capillary radius.

Hench [1], and Wallace and Hench [3] proposed addition of drying control chemical additives (DCCAs) to the solvent in order to decrease ΔP. They successfully obtained a large crack-free dry silica gel body by using formamide as a DCCA. They concluded that the DCCA had a role in increasing the pore radius, since the dry gel obtained had larger and more uniform pore radii than those in a DCCA-free gel.

On the other hand, Adachi and Sakka [4, 5] intended to decrease the surface tension, γ, by using *N,N*-dimethylformamide (DMF) as a DCCA and they also obtained a crack-free dry gel. They considered that in the drying process the components of the solvent must have evaporated according to the order of the lowest boiling point, i.e. ethanol first, then water and DMF last. ΔP then decreased, since DMF had a lowered surface tension.

The aim of this work was to study the chemical effect of DCCAs on the sol–gel reaction process, i.e. the growth of silica particles during the hydrolysis and condensation reaction, gelation time and physical properties of the dry gel. Usually DCCA is added to the solution with comparable amount to silicon alkoxide, however, to investigate the chemical effect of DCCA, the DCCA:silicon alkoxide ratio was varied from 0.1 to 1.5 in this study.

DMF, *N,N*-dimethylacetamide (DMA) and ethylene glycol (EG) were studied as DCCAs. A two-step silica sol–gel process, in which both acidic and basic catalysts were used and the efficiency of hydrolysis was expected to be high [6], was adopted for gel preparation. The growing process of silica particles was observed by transmission electron microscopy (TEM).

2. Experimental procedure

2.1. Gelation

A two-step silica sol–gel process was adopted for gel preparation. A process with an acid and a base catalysed step was proposed by Brinker *et al.* [6]. In the first step $Si(OR)_4$ molecules were hydrolysed to give $Si(OR)_3(OH)$ uniformly dispersed by acidic catalyst; in the second step $Si(OR)_3(OH)$ molecules were completely hydrolysed to give $Si(OH)_4$ by basic catalyst. Using this process the reaction efficiency could be improved and the reaction time reduced. Tetraethoxyorthosilicate (TEOS) was utilized as a starting material. The composition of the solution is expressed as the ratio of TEOS:ethanol:H_2O (in 10^{-2} M HCl + 10^{-1} M NH_4OH); for instance 1.0:2.0:2.0 (1.0 + 1.0).

The experimental flow chart is shown in Fig. 1. TEOS, ethanol and DCCA were measured in a flask and kept at 30 °C by stirring in a water bath – this was solution A. The acid–ethanol solution (solution B) in which 10^{-2} M HCl aqueous solution was mixed with the same weight of ethanol was added slowly over 2 min to solution A. The solution was stirred for 1 h. This was the first-step hydrolysis reaction time (t_H). After this step, the base–ethanol solution (solution C)

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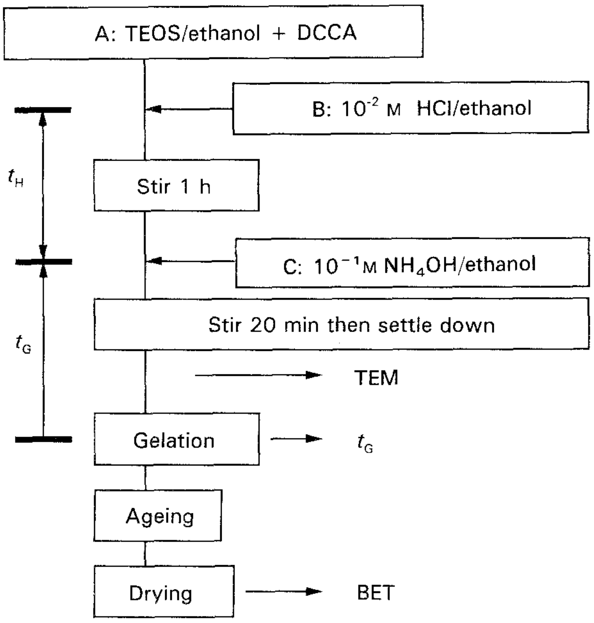

Figure 1 Experimental flow chart.

in which 10^{-1} M ammonium hydroxide aqueous solution was mixed with the same weight of ethanol added slowly over 2 min to the solution. After 30 min of stirring the solution was moved to small glass bottle and sealed. It was kept at 30 °C until gelation occurred. Gelation time (t_G) is defined as the time from the finish of the addition of solution C ($t = 0$) to gelation. Gelation was confirmed by tilting the flask and observing no fluidity in the sample. Following gelation the sample was aged for 7–20 days at room temperature. A cubic sample of 1 cm^3 was cut from the aged gel and was dried in an electric oven: the heating program was increasing the temperature at the rate of 1 °C h^{-1} to 200 °C, holding for 24 h at 200 °C and decreasing the temperature to room temperature in 3 h. The crack development was confirmed by visual inspection. The dry gel was ground and supplied for BET specific area measurement (N_2 adsorption, Micromeritics Flowsorb 2300, Simadzu, Japan).

2.2. TEM observation

For direct observation of growing silica particles TEM (TEM: JEM-200CX, JEOL, Japan) was used. After the addition of solution C a small portion of the solution was extracted by pipette and an excess of ethanol added to terminate the reaction. After 1 min of stirring a microgrid (ϕ 3 mm: Oukenshouji, Japan) was dipped once into the solution and dried naturally to prepare the specimen for TEM observation. Diameters of the silica particles were determined as a mean value of the measured diameters on the TEM images. The extractions were performed at reduced times, $t/t_G = 0.14$, 0.27, 0.41 and 0.54.

3. Results

3.1. Silica particles

Fig. 2 shows the TEM images of the silica particles at $t/t_G = 0.45$ for DCCA free solution and $t/t_G = 0.54$ for the solutions to which DMF, DMA and EG were added as DCCAs. The general composition of the solutions was 1:2:2 (1 + 1). The particles in the DCCA free solution were spherical and uniform, on the other hand, particles in the DCCA added solutions had deformed shapes and inner structures. In particular, the particle in the EG added solution (Fig. 3) was composed of smaller primary particles. The size of the primary particles was estimated to be 3–4 nm.

The relationships between the size of isolated particles in the TEM image and the reduced time, t/t_G, are shown in Fig. 4. The particle sizes in the DCCA free and the EG added solutions increased linearly with t/t_G, while those in DMF and DMA added solutions increased gently and parabolically. All DCCAs suppressed the growth of silica particles.

3.2. Dry gel

The compositions of the solutions, gelation time, specific surface areas (SA) and BET radius of the dry gels and development of the cracks are summarized in Table I. In this study, crack-free dry gel monoliths were obtained only from the DMA added solutions. The molar ratios of H_2O and DCCA were considerably smaller than those used by other researchers [1, 3–5]. This could be attributed to the two-step silica sol–gel process and the characteristics of DMA

3.2.1. Gelation time

Fig. 5 shows the relation between the gelation time and DCCA addition. The general composition of the solutions was 1:2:2 (1 + 1). Addition of DMA decreased the gelation time until it reached 0.3 in molar ratio, gelation time increased over 0.3. The addition of DMF moderately increased the gelation time. The addition of EG decreased gelation time.

3.2.2. Specific surface area and BET radius

Fig. 6 shows the relation between the SA of dry gel and of DCCA addition. The general composition of the solutions was 1:2:2 (1 + 1). The addition of DMF increased the SA of the dry gel linearly. On the other hand, addition of DMA decreased the SA. The addition of EG decreased the SA extensively until 0.2 in molar ratio, subsequent increases increased the SA.

Assuming that the primary particle had a spherical shape, the BET radius could be calculated from the specific area according to

$$d = C/(\rho_m SA) \qquad (2)$$

where d is the BET radius in m, constant $C = 6$ for free spheres. If the density of the material, ρ_m is expressed in kg m^{-3}, SA is the specific surface area in m^2 kg^{-1}. $\rho_m = 2.2 \times 10^{-6}$ kg m^{-3} [7] was used in this work. Equation 2 means that the smaller the specific surface area becomes the larger the BET radius grows.

The BET radii of the obtained dry gels were in the range of 3.00–4.55 nm. If the value represented the primary particle size in the dry gel then it was in

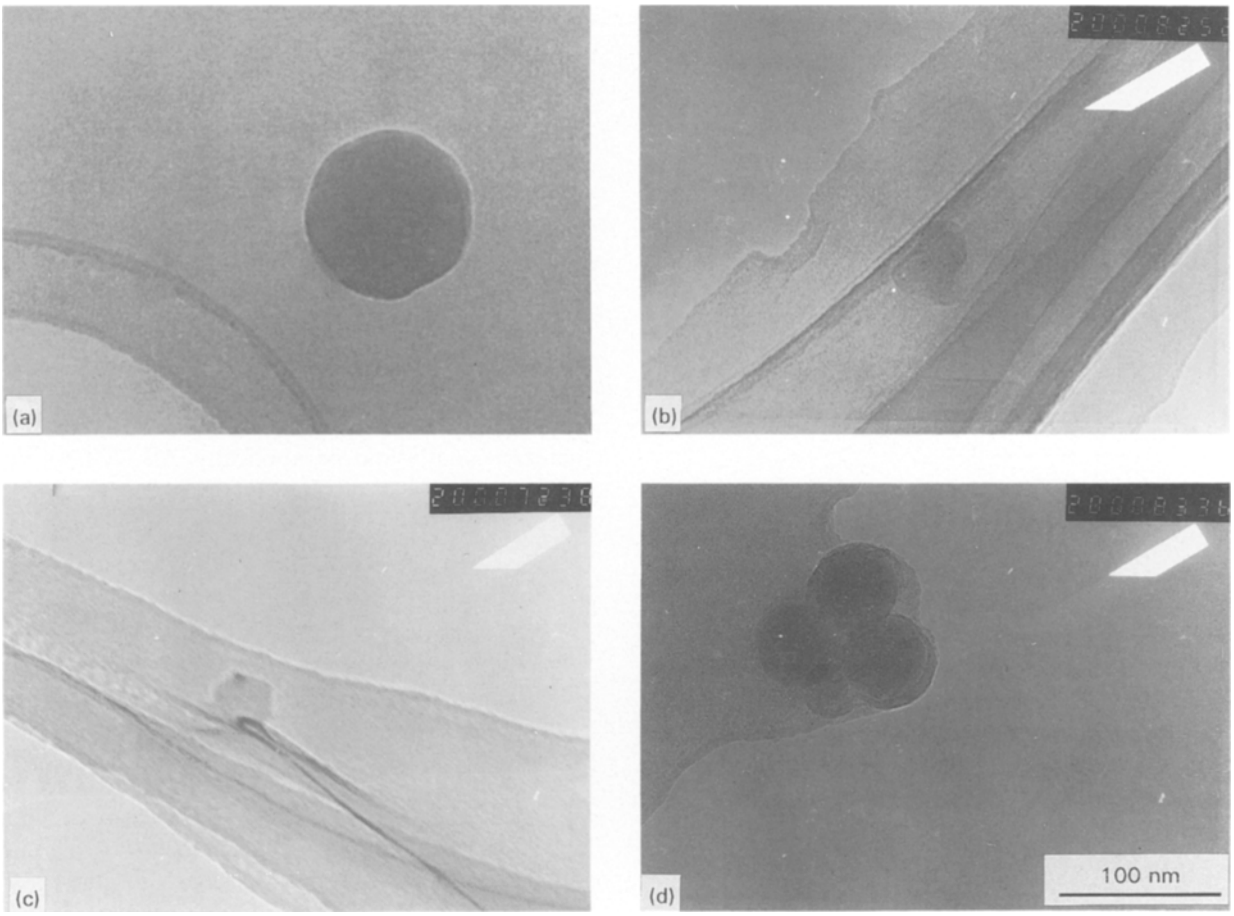

Figure 2 Growing silica particles in the solutions examined with TEM. TEOS: ethanol:H_2O = 1:2:2 (1 + 1). (a) DCCA free, $t/t_G = 0.60$; (b) DMF molar ratio = 0.3, $t/t_G = 0.54$; (c) DMA molar ratio = 0.3, $t/t_G = 0.54$; (d) EG molar ratio = 0.3, $t/t_G = 0.54$.

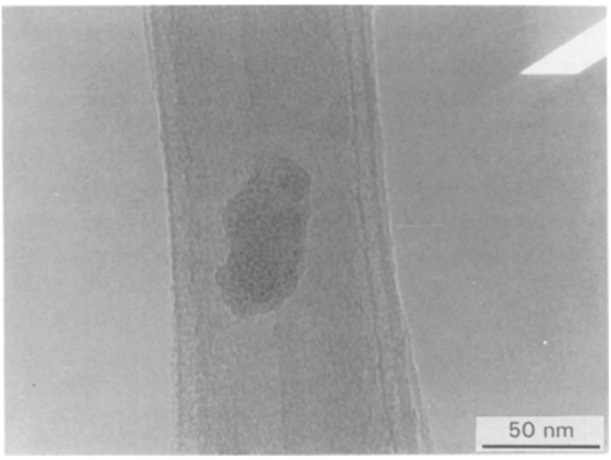

Figure 3 TEM image of silica particles at $t/t_G = 0.54$ in the solution to which EG in the molar ratio 0.3 was added.

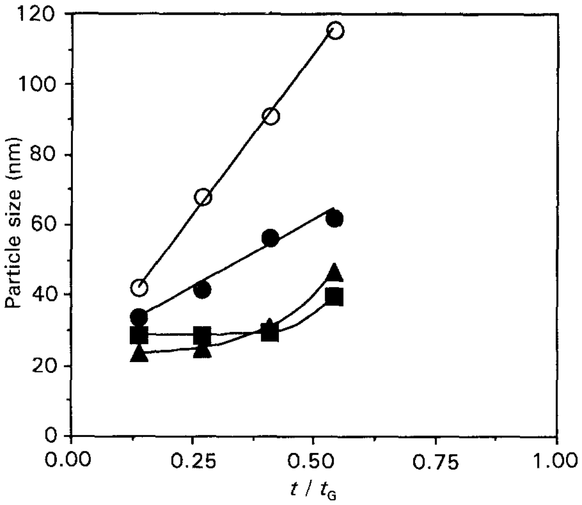

Figure 4 Growth of silica particle with t/t_G. TEOS: ethanol:H_2O = 1:2:2 (1 + 1). ○, DCCA free; ▲, DMF molar ratio = 0.3; ■, DMA molar ratio = 0.3; ●, EG molar ratio = 0.3.

agreement with the estimated radius of primary particles from the TEM image in Fig. 3.

The crack-free gels had relatively large BET radii (Table I). The gels to which EG was added had rather large BET radii, however, they broke down into small pieces.

4. Discussion

The comparison of the silica particle radii (obtained from TEM images) and BET radii suggested that the silica particles in all of the solutions, i.e. DCCA free, DMF, DMA and EG added, were secondary particles formed by agglomeration of primary particle, as mentioned by Hench and West [8]. Consequently, the gelation process could be described as: (1) growth of primary particle; (2) agglomeration of the primary particles and growth of the secondary particles; (3) formation of linkages between secondary particles; (4) gelation. DCCA enhanced the growth of primary

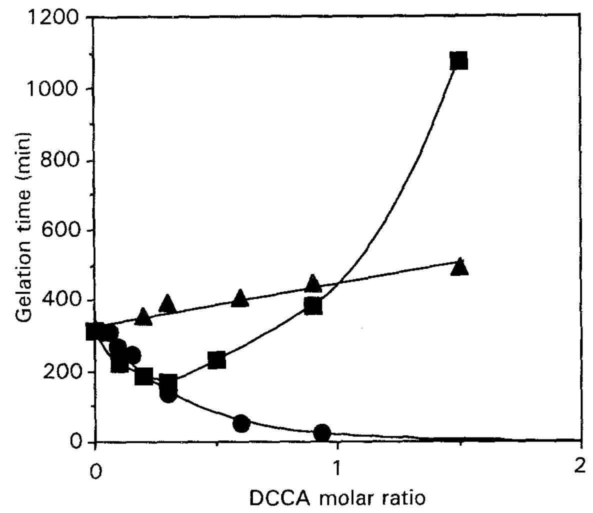

Figure 5 The effect of DCCA addition on the gelation time (t_G). ▲, DMF; ■, DMA; ●, EG.

particles and suppressed the agglomeration of them. Gelation could be accelerated or decelerated by DCCA addition.

In spite of the addition of DMF, and of a large BET radius in EG added gel, a crack-free dry gel could not be obtained for these systems. This suggested that decreasing the surface tension of the solution and increasing the pore size were necessary but were not sufficient to obtain a crack-free dry gel.

Addition of DCCA strongly affected the structure of the obtained silica gel as seen by the shape of silica particles in the TEM image, i.e. secondary particles were distorted spheres; also the growth of the particles was suppressed by the addition of DCCA. So, the critical roles of DCCAs should be to provide uniform pore radii and to construct a strong gel structure which could resist the drying stress.

5. Summary

The chemical effects of DMF, DMA and EG as DCCAs were examined in a two-step silica sol–gel process. Crack-free dry gel was obtained only through the solution to which DMA was added. In that case, the ratios of H_2O and DCCA were smaller than in other researchers work. The results showed that optimum conditions were required for the application of DCCAs.

TABLE I Composition of the solutions, gelation time, specific surface areas (SA) and BET radius of the dry gels and development of cracks

Molar ratio			DCCA	Molar ratio	t_G (min)	SA[b] (m^2/g)	BET radius (nm)	Crack[c]
TEOS	Ethanol	H_2O[a]						
1	2	2	Free	0.0	316	830.13	3.29	× ×
1	2	2.5	Free	0.0	144	810.20	3.27	× ×
1	2	3	Free	0.0	80	755.00	3.52	× ×
1	2	2	DMF	0.1	268	843.70	3.23	×
1	2	2	DMF	0.2	356	795.85	3.43	×
1	2	2	DMF	0.3	391	908.33	3.00	×
1	2	2	DMF	0.6	406	891.56	3.06	×
1	2	2	DMF	0.9	448	963.10	2.83	×
1	2	2	DMF	1.5	493	974.67	2.80	×
1	2	2	DMA	0.1	220	919.40	2.97	×
1	2	2	DMA	0.2	186	792.48	3.44	×
1	2	2	DMA	0.3	165	834.25	3.27	×
1	2	2	DMA	0.5	230	798.11	3.42	×
1	2	2	DMA	0.9	384	770.62	3.54	○
1	2	2	DMA	1.5	1076	731.16	3.73	△
1	2	2.5	DMA	0.1	83	860.37	3.17	△
1	2	2.5	DMA	0.2	61	856.62	3.18	△
1	2	2.5	DMA	0.3	87	813.74	3.35	○
1	2	2.5	DMA	0.5	110	838.72	3.25	○
1	2	2.5	DMA	0.9	215	776.19	3.51	○
1	2	2.5	DMA	1.5	408	703.03	3.88	△
1	2	3	DMA	0.1	34	769.57	3.54	×
1	2	3	DMA	0.2	34	670.65	4.07	○
1	2	3	DMA	0.3	71	690.70	3.95	△
1	2	3	DMA	0.5	67	793.52	3.44	△
1	2	3	DMA	0.9	159	684.66	3.98	○
1	2	3	DMA	1.5	372	780.82	3.49	△
1	2	2	EG	0.03	310	737.90	3.70	× ×
1	2	2	EG	0.06	307	732.21	3.72	× ×
1	2	2	EG	0.09	270	652.22	4.18	× ×
1	2	2	EG	0.15	244	597.08	4.57	× ×
1	2	2	EG	0.3	135	647.47	4.21	× ×
1	2	2	EG	0.6	53	766.88	3.56	×
1	2	2	EG	0.93	23	773.05	3.53	×

[a] Total amount of H_2O: [b] specific surface area: [c] ○, no crack; △, a few cracks, ×, intensive cracking; × ×, break down to small pieces.

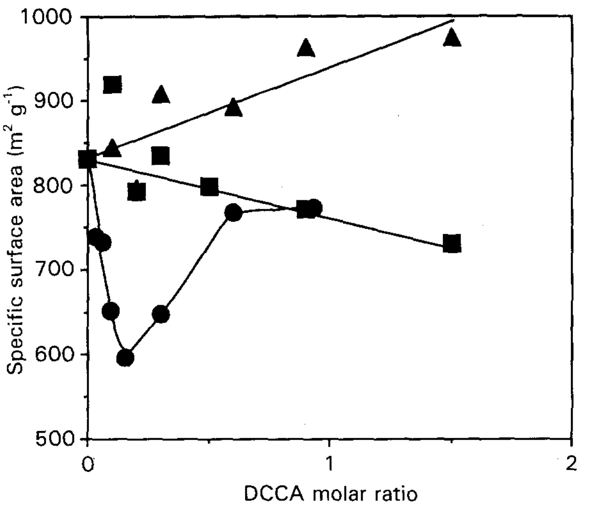

Figure 6 The effect of DCCA addition on the specific surface area (SA) of dry gels. ▲, DMF; ■, DMA; ●, EG.

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