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Preparation of monolithic silica gel and glass by the sol–gel method using N,N-dimethylformamide

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The use of N,N-dimethylformamide (DMF) was found to be effective in the sol–gel synthesis of silica gel and glass monoliths from tetramethoxysilane (TMOS) by the sol–gel method. Wet gel bodies prepared by gelation of TMOS–DMF–CH_3OH–H_2O–NH_4OH (or HNO_3) solutions could be dried without the occurrence of fracture or cracks when drying conditions were appropriate. Furthermore, the resultant dried gel monoliths could be converted without cracking or bloating to silica glass on heating up to 1050° C and holding there for 2 h, when the composition of the starting solution was appropriate.

1. Introduction

The most serious problems encountered in the sol–gel preparation of silica glass monoliths are crack formation or fracture [1] taking place in the process of drying wet gels, and crack formation and bloating [2] observed on heating to convert dried gels to silica glass. Wallace and Hench [3, 4] proposed the use of a drying control chemical additive (DCCA) to avoid crack formation in the process of drying wet gels for producing large dried gel monoliths. They used formamide as an effective DCCA.

This paper reports the application of N,N-dimethylformamide (DMF), a new DCCA, which has been found effective in producing not only large silica gel monoliths but also silica glass monoliths without the occurrence of cracks, fracture and bloating.

2. Experimental procedure

2.1. Preparation of the starting solution and gelation

A mixture of tetramethoxysilane (TMOS) and a desired amount of DMF was prepared. To this mixture, a mixture of water, methanol and catalyst (ammonia or nitric acid) was added dropwise under stirring at room temperature. The resulting homogeneous solution was put in a polymethylpentene cylinder of diameter 37 mm and length 245 mm, covered with aluminium foil and subjected to the hydrolysis–polycondensation reaction leading to gelation in an oven. The temperature was kept at 35° C when catalysed with ammonia and at 60° C when catalysed with nitric acid, so that the gelation might take place not too fast and not too slowly. The wet gels obtained were aged by raising the oven temperature to 80° C in 48 h.

2.2. Drying of the wet gel

For drying, the wet gels were placed in a drying box and the temperature was raised to 80° C. At this temperature the drying was started by perforating the cover of aluminium foil with a few pinholes 1 mm in diameter. The gel was kept at this temperature for 24 h. Thus dried gels were obtained.

2.3. Sintering of the dried gel

The dried gels were sintered in an alumina crucible in an air atmosphere in an electrically heating furnace. The temperature was raised at a rate of 25° C h^{-1}. The samples were taken out of the furnace at desired temperatures and tested by various measurements. In order to obtain well-sintered silica glasses, the dried gels were heated up to 1050° C at a rate of 20° C h^{-1} and kept at this temperature for 2 h.

2.4. Measurements of the density and hardness and electron microscopic observation

The bulk densities of dried gels and partially sintered porous gels were estimated by measuring the volume and weight of a disc gel specimen. Discs of about 10 mm thickness, cut from the gel rod of diameter about 21 mm, were used for the measurements. The densities of well-sintered, non-porous glasses were measured at 25° C by the pycnometer method using water as the replacing liquid.

The microhardness of the gels and glasses was measured with an Akashi Manufacturing Co. (Japan) Type MVK-E microhardness tester. The load was changed from 20 g to 500 g so that the size of indentation might be nearly constant.

The microstructure of gels and glasses was observed with a Hitachi Type S-450 scanning electron microscope. The fracture surfaces of gels and glasses with Pt–Pd vapour-deposited film were observed.

3. Results and discussion

In order to give the general concept in the present process, pictures showing the starting solution, wet gel, dried gel and finished SiO_2 glass are shown in Fig. 1. The starting solution and the wet gel are

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TABLE I Properties of a gel and glass prepared from a starting solution of the composition $1TMOS–1DMF–2.2CH_3OH–10H_2O–3.7 \times 10^{-4}NH_4OH$

Surface properties of the dried gel:	
Specific surface area	$620\,m^2\,g^{-1}$
Bulk density	$0.64\,g\,cm^{-3}$
Hardness of the dried gel heated to:	
700° C	$10\,kg\,mm^{-2}$
1000° C	$46\,kg\,mm^{-2}$
1050° C	$250\,kg\,mm^{-2}$
1050° C (after heating for 2 h)	$534\,kg\,mm^{-2}$

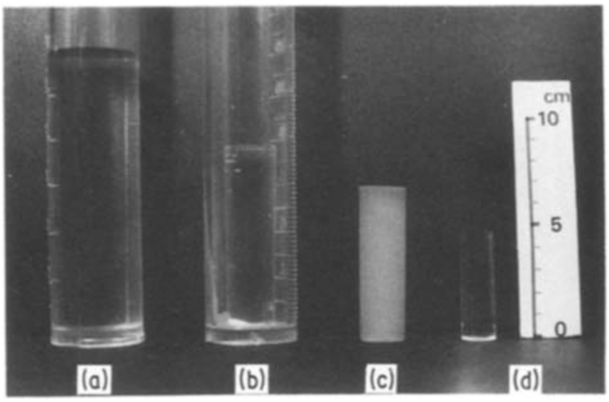


Figure 1 Photographs of gel and glass prepared from the starting solution $1TMOS:1DMF:2.2CH_3OH:10H_2O:3.7 \times 10^{-4}NH_4OH$. (a) Starting solution, (b) wet gel, (c) dry gel, (d) glass.

transparent because no pores are present or the pores are filled with liquid. The dried gel is translucent, because of the presence of a large volume percentage of pores without liquid. The sintering by heating to about 1050° C changes the dried gel to a transparent silica glass, as shown in Fig. 1d, if the composition of the starting solution and preparation conditions are appropriate. Some properties of dried gel and glass prepared from a typical solution are shown in Table I.

3.1. Formation of dried gel monoliths

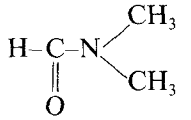
The compositions of the starting solutions in the $TMOS–DMF–CH_3OH–H_2O–NH_4OH$ (or HNO_3) system, which can be successfully changed into a dried gel monolith without cracks, are shown in Table II. The gelation times are also shown.

It is seen that both NH_4OH and HNO_3 as catalysts work in producing monolithic dried gel with no cracks. A monolithic dried gel without cracks was not formed, however, when no catalyst was added, indicating that the use of catalyst is obligatory. Comparison of Nos 1, 2 and 3 in Table II shows that the NH_4OH concentration affects the gelation time of the solution. The gelation time of No. 3 is very short at a few minutes; gelation takes place before a sufficient stirring, but it is noticeable that the dried gel is obtained without crack formation.

Nos 4, 5 and 6 indicate that a monolithic dried gel is obtained over a wide range of $[H_2O]/[TMOS]$ ratio. The markedly long gelation time for No. 4 suggests that the small value of 2 for the $[H_2O]/[TMOS]$ ratio is a minimum water content required for hydrolysis, so that the subsequent polycondensation is limited.

It was found that in the present systems dried monolithic gels of high porosity were obtained irrespective of the kind of catalyst, that is with both ammonia and nitric acid. Nogami and Moriya [5] showed that a very high porosity corresponding to a bulk density of less than $1.0\,g\,cm^{-3}$ was obtained with NH_4OH, whereas a low porosity corresponding to a bulk density higher than $1.5\,g\,cm^{-3}$ was obtained with an acidic catalyst. The bulk density of the present dried gels ranged from 0.57 to $0.99\,g\,cm^{-3}$. The high porosity shown in Table I and the large pores may be responsible for the opaqueness of the dried gels.

The structural formula of DMF is expressed as



This is derived from formamide by replacing the two hydrogens in the amide group by methyl groups and it does not form hydrogen bonds, in contrast with formamide. Therefore, the boiling point of DMF is lower at 153° C than that of formamide (210° C). This makes it possible to dry the wet gels prepared from DMF-containing solutions by heating at 150° C as described above. Artaki *et al.* [6] attributed the formation of low bulk density gels from formamide-containing solutions to strong hydrogen bonding by formamide. The present result indicates that DMF which cannot make hydrogen bonds also gives low bulk density gels.

3.2. Sintering of dried gel monoliths

Figs 2 and 3 show the increase of the density and the

TABLE II Compositions of the starting solutions which can form a monolithic gel without cracks

No.	Molar ratio						Gelation time (h)
	TMOS	DMF	CH_3OH	H_2O	NH_4OH	HNO_3	
1	1	1	2.2	10	3.7×10^{-4}	–	4.4
2	1	1	2.2	10	7.4×10^{-4}	–	5.6
3	1	1	2.2	10	3.7×10^{-3}	–	0.05
4	1	1.4	2.7	2	3.7×10^{-4}	–	96.0
5	1	1.4	2.7	10	3.7×10^{-4}	–	7.5
6	1	1.4	2.7	20	3.7×10^{-4}	–	4.1
7	1	2	5.5	2	–	0.05	8.6
8	1	2	1.9	10	–	0.05	5.2

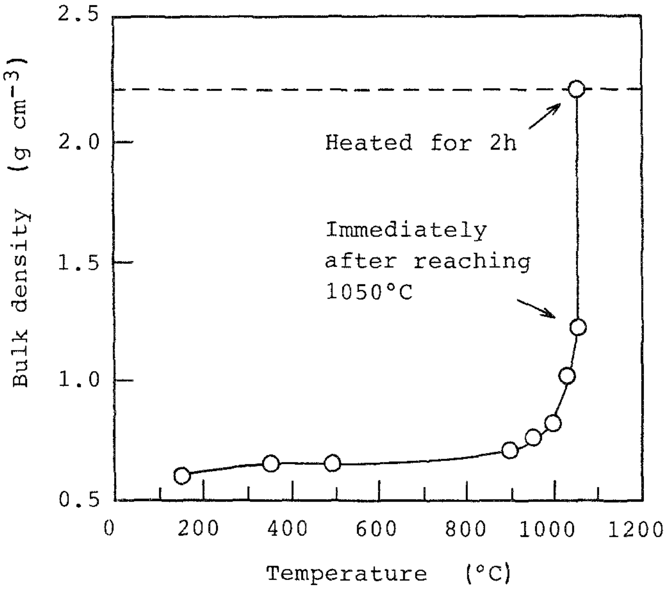


Figure 2 Change in bulk density of the dry gel with sintering temperature. The broken line indicates the density of vitreous silica (2.20 g cm^{-3}). The composition of the starting solution was 1TMOS : 1DMF : 2.2CH_3OH : 10H_2O : 3.7 × $10^{-4}NH_4OH$.

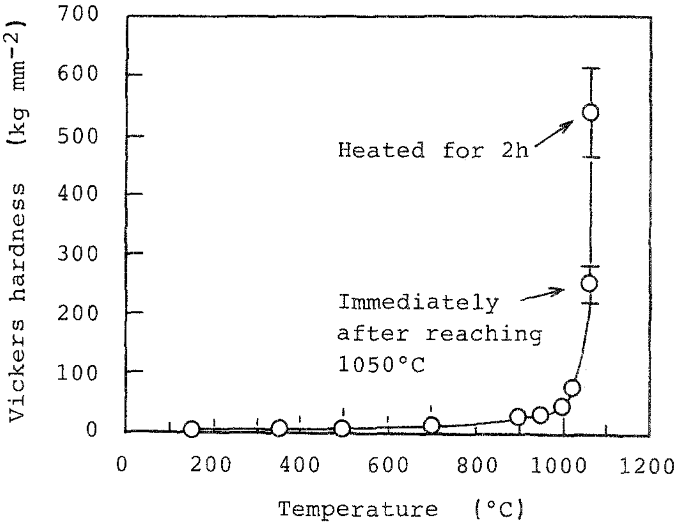


Figure 3 Change in Vickers hardness of the dry gel with sintering temperature. The composition of the starting solution was 1TMOS : 1DMF : 2.2CH_3OH : 10H_2O : 3.7 × $10^{-4}NH_4OH$.

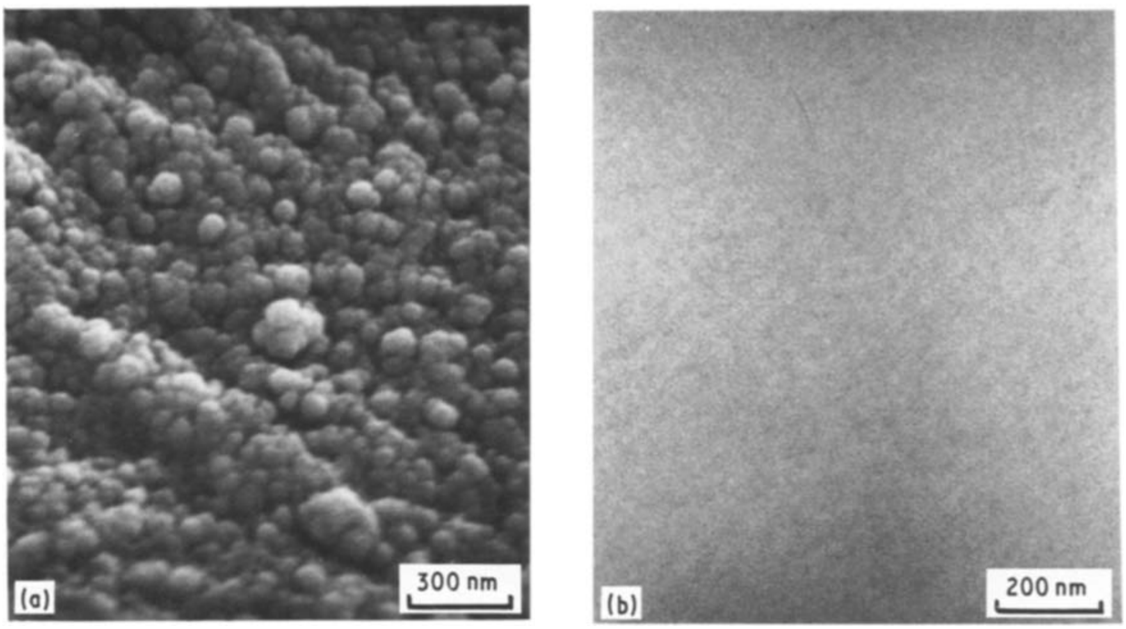


Figure 4 SEM micrographs of the fractured surfaces of gels (a) dried at 150°C and (b) sintered for 2 h at 1050°C, prepared from the solution 1TMOS : 1DMF : 2.2CH_3OH : 10H_2O : 3.7 × $10^{-4}NH_4OH$.

Vickers hardness, respectively, with heating temperature for dried gel prepared from a starting solution of composition 1TMOS : 1DMF : 2.2CH_3OH : 10H_2O : $7.4 \times 10^{-4}$$NH_4OH$ in mole ratio. The bulk density of the dried gel was $0.626\,g\,cm^{-3}$.

It is seen from the figures that both the bulk density and Vickers hardness increase slowly up to 950 to 1000° C and then very sharply up to 1050° C. The Vickers hardness of the dried gel heated up to 700, 1000 and 1050° C is shown in Table I.

Immediately after reaching 1050° C, however, the bulk density and the Vickers hardness of the gel are $1.23\,g\,cm^{-3}$ and $260\,kg\,mm^{-2}$, respectively, about half the values for quartz glass prepared by melting. The density and the Vickers hardness of the latter are $2.20\,g\,cm^{-3}$ and $650\,kg\,mm^{-2}$, respectively. After heating at 1050° C for 2 h the gel becomes transparent, indicating that the gel has become a glass. Its density and hardness are very close to those for the melt-derived quartz glass.

Scanning electron microscopic pictures of the fracture surface of the dried gel and the glass prepared by sintering are shown in Fig. 4. The dried gel shows a microstructure consisting of spherical particles of diameter 30 to 100 nm. The particles are densely packed and it appears that particles are strongly bonded with each other through their faces, making the framework structure of the gel strong. This explains why dried gels without cracks are obtained in the present system.

SEM pictures of the fracture surface of the transparent glass obtained by heating at 1050° C shows no particulate structure, indicating that the dried gel has changed into a silica glass of uniform structure.

4. Summary

Solutions of TMOS–DMF–CH_3OH–H_2O–NH_4OH (or HNO_3) of appropriate compositions were gelled by reacting at 35 or 60° C and aged at 80° C, and the resulting wet gels could be changed to dry gels without fracture and cracks by heating slowly to 150° C. It was found that the use of DMF together with a catalyst, ammonia or nitric acid, was necessary to produce crack-free gel monoliths. When the composition of the starting solution was appropriate, the dried monoliths could be converted to silica glass monoliths without crack formation or bloating by heating up to 1050° C in an air atmosphere.

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