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Preparation of silica monolith via sol-gel route

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Abstract. The present investigation deals with the synthesis of monolithic $NiCl_2$-silica gels obtained by hydrolysis and polycondensation of tetraethoxy silanes. This sol to gel formation can mainly be controlled by adjusting some variables e.g. acid content of the solution, ageing and leaching times. A minimum acid content was found necessary to prepare uncracked gel while ageing and leaching times were found to be not that sensitive for the formation of uncracked gels.

Keywords. Monolith; sol-gel.

1. Introduction

Sol-gel processing has presently become the most modern approach for inorganic hybrid material development because of its simplicity and effectiveness (Mackenzie 1988; Ganguli 1989). During the last few years, extensive research has been carried out to prepare glass-metal micro/nanocomposites without melting via the sol-gel-route by *in situ* reduction of metallic salts in the silica gel matrix (Das *et al* 1990; Basumallick *et al* 1993). In spite of this phenomenal development, the use of this new class of materials in commercial and technological exploitation as superparamagnetic materials, substrates of semiconduction technology, optical communication, photothermal conversion devices and others are few and an urge to prepare these composites in the monolithic forms has now bloomed into a valid commercial proposition in many cases. The drying of gel is severely handicapped by cracking problems. This is caused mainly by the stresses due to capillary force arising from solvent-gel interfacial tension during drying. It is reported in the literature (De *et al* 1990) that for monolith, the proportion of acid should substantially be controlled within catalytic amounts (0·4–0·7 mol per mole of alkoxide) leading to interesting final products. Though the acid is a must in the initial stages, its removal by washing is an essential prerequisite for obtaining monolithicity. The water and TEOS content of the starting solution should be in the ratio of 10:1 on molar basis. After gelling, the higher the ageing time, the higher will be the polycondensation leading to more rigid structure which is likely to withstand more drying stress and hence it is expected that it will affect the formation of monolithic gel. So it is important to know, to what extent the parameters such as acid content, ageing and leaching times are significant for the formation of monolithic gel. In this paper we report the result on the relative importance of these above factors for controlling the monolithicity during drying of gel.

2. Experimental

Virgin gel samples were prepared with the compositions as given in table 1.

A homogeneous solution of double distilled water and requisite amount of 8(N) HCl is thoroughly made. This solution is then added dropwise into a beaker containing TEOS of Fluka made (>98%) placed upon a magnetic stirrer with the reaction temperature controlled at 22°–24°C. The resulting solution is left for gelling at room temperature after transferring it to a glass cylinder of 2·5 cm diameter. Gelation of the sols prepared in this way occurs within one or two days. The time interval between gelling and addition of water for leaching out the acid is the ageing time. The ageing time was varied within range of 24 h to 72 h. After ageing the gel sample is dipped in double distilled water of 30 c.c. This water is decanted after 24 h and its pH level noted. Again 30 c.c. of double distilled water is poured and the above process is repeated. The leaching time is varied over 4 to 8 days. After leaching one set of gel, samples are immersed in concentrated $NiCl_2$ and glucose solution for a few days when diffusion of $NiCl_2$ and glucose into the gels occurs. The excess solution decanted and the samples prepared as above are kept in ordinary atmosphere and temperature for a few days. Ultimately, the samples are dried at 60°C in an oven for 10 days (6 h each day).

After drying it was noted visually which sample had cracked and which had not.

3. Results and discussion

Tables 2–4 summarize the effect of 8(N) HCl content, ageing time and leaching time on the monolithic behaviour of gel samples after drying. Tables 5–7 represent the

Table 1. Composition of gel.

Composition	TEOS (c.c.)	Mol. ratio TEOS:H_2O	Double distilled water (c.c.)	8(N) HCl (c.c.)	Mol. ratio TEOS:HCl
1	5	1:17	5·5	1·5	1:0·54
2	5	1:17	5·0	2·0	1:0·72
3	5	1:17	4·5	2·5	1:0·90

Table 2. Effect of ageing and leaching time on the cracking behaviour of silica gel for 1·5 c.c. 8(N) HCl content during drying.

Ageing time (h) ↓	Leaching time (days)→	4	6	8	Number of samples uncracked
24		Uncracked	Uncracked	Cracked	2
48		Cracked	Cracked	Uncracked	1
72		Uncracked	Cracked	Cracked slightly	2
Number of samples uncracked		2	1	2	5

Table 3. Effect of ageing and leaching time on the cracking behaviour of silica gel for 2·2 c.c. 8(N) HCl content during drying.

Ageing time (h) ↓	Leaching time (days) → 4	6	8	Number of samples uncracked
24	Cracked	Uncracked	Cracked	1
48	Cracked	Uncracked	Uncracked	2
72	Uncracked	Cracked	Uncracked	2
Number of samples uncracked	1	2	2	5

Table 4. Effect of ageing and leaching time on the cracking behaviour of silica gel for 2·5 c.c. 8(N) HCl content during drying.

Ageing time (h) ↓	Leaching time (days) → 4	6	8	Number of samples uncracked
24	Uncracked	Uncracked	Cracked slightly	3
48	Uncracked	Uncracked	Uncracked	3
72	Uncracked	Uncracked	Cracked slightly	3
Number of samples uncracked	3	3	3	9

Table 5. Measurement of pH on days of leaching for HCl content 1·5 c.c.

Sample No.	Leaching days 1	2	3	4	5	6	7	8
1	0·67	1·16	1·90	3·30	—	—	—	—
2	0·59	1·24	1·87	2·60	—	—	—	—
3	0·41	1·07	1·75	2·35	—	—	—	—
4	0·75	0·90	1·22	1·65	2·04	2·60	—	—
5	0·37	0·85	1·77	2·20	2·88	3·49	—	—
6	0·55	1·21	1·64	2·25	2·95	3·74	—	—
7	0·33	0·82	1·48	2·17	2·83	3·53	4·53	5·70
8	0·38	0·95	1·64	2·30	2·98	3·76	4·90	5·60
9	0·40	0·96	1·57	2·24	2·89	3·67	5·07	6·11

variation of pH of leached out solution as a function of leaching time for various gel samples prepared with different acid contents. Tables 2 and 3 recorded the samples prepared with 1·5 c.c. and 2 c.c. of 8(N) HCl and show that slightly above 50% of gel samples remain in the monolith form while almost 100% of the gel samples made with 2·5 c.c. of 8(N) HCl remain in the monolithic form (refer table 4). This suggests that in order to get gel monolith after drying, higher acid content is a must. However, the role of neither leaching time nor ageing time is decidingly significant (tables 2–4). It is reported that (De *et al* 1990) if the acid with which the gels are prepared is not leached out, the gel samples invariably cracked after drying. This implies that higher acid

Table 6. Measurement of pH on days of leaching for HCl content 2·0 c.c. 8(N).

Sample No	Leaching days	1	2	3	4	5	6	7	8
1		0·63	1·12	1·82	3·32	—	—	—	—
2		0·60	1·25	1·90	2·66	—	—	—	—
3		0·36	1·06	1·73	2·35	—	—	—	—
4		0·62	0·89	1·24	1·71	2·18	2·75	—	—
5		0·31	0·90	1·63	2·12	2·79	3·35	—	—
6		0·48	1·09	1·51	2·12	2·78	3·49	—	—
7		0·26	0·78	1·41	2·09	2·75	3·41	4·16	5·65
8		0·28	0·83	1·50	2·12	2·73	3·40	4·17	4·80
9		0·34	0·86	1·45	2·10	2·74	3·48	4·31	6·07

Table 7. Measurement of pH on days of leaching for HCl content = 2·5 c.c. 8(N).

Sample No	Leaching days	1	2	3	4	5	6	7	8
1		0·60	0·97	1·65	2·82	—	—	—	—
2		0·55	0·99	1·57	2·28	—	—	—	—
3		0·30	0·97	1·61	2·19	—	—	—	—
4		0·54	0·81	1·10	1·52	1·92	2·48	—	—
5		0·23	0·86	1·50	1·95	2·56	3·16	—	—
6		0·41	0·97	1·37	1·97	2·57	3·22	—	—
7		0·17	0·69	1·29	1·95	2·57	3·17	4·02	5·22
8		0·20	0·75	1·40	1·98	2·57	3·23	3·84	4·60
9		0·26	0·78	1·30	1·90	2·57	3·29	3·81	5·89

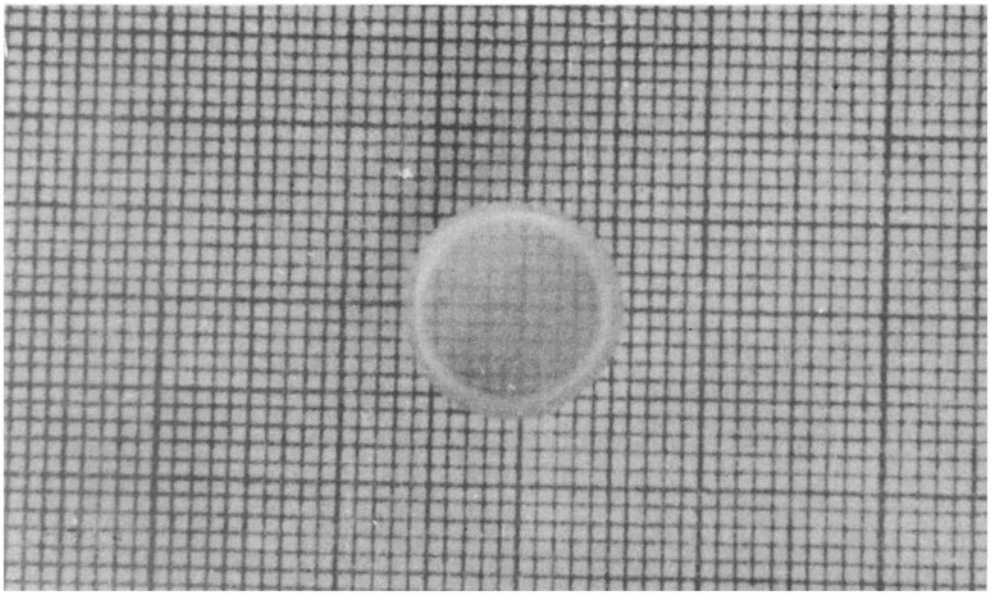

Figure 1. Optical photograph of virgin silica gel of sample no. 2 after drying, subjected to ageing for 48 h followed by 6 days of leaching.

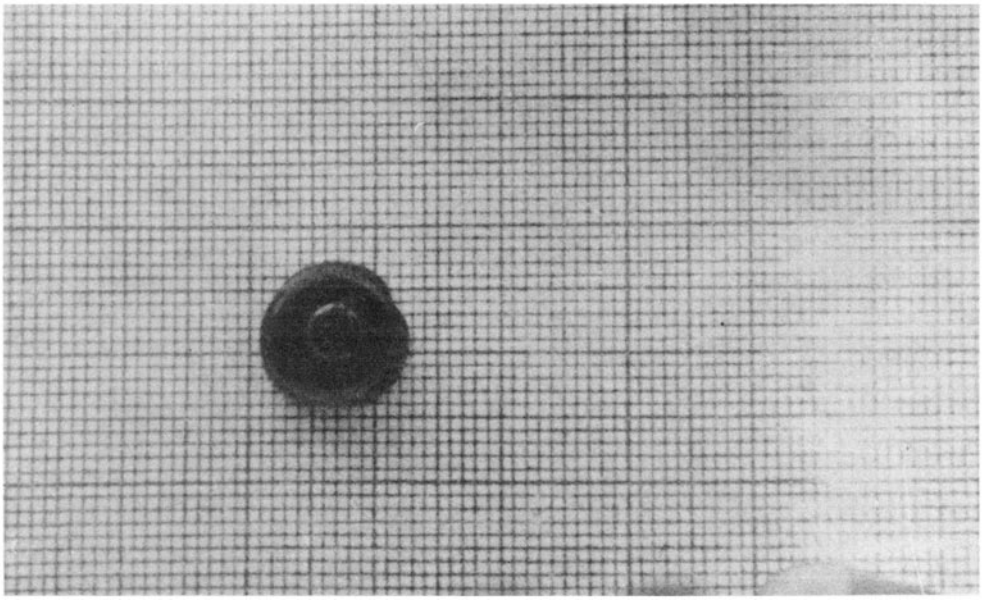

Figure 2. Optical photograph of silica gel of sample no. 3 containing $NiCl_2$ and $C_6H_{12}O_6$ after drying, subjected to ageing for 72 h followed by 6 days of leaching.

content after formation of the gel is detrimental during drying and causes fracture. This is the reason why one should leach out the acid in the gel before putting to drying. Tables 5–7 show that the pH of aqueous solution after 4 days of leaching is around 2. Since the days of leaching beyond 4 days are not conclusively significant (tables 2–4), whatever acid left after 4 days of leaching is not significant in promoting fracture in the gel during drying. It is expected that with higher ageing time the polycondensation becomes more which should make the structure stronger to withstand drying stress. However, the gain in strength for ageing time up to 72 h is not always sufficient to avoid fracture.

Figures 1 and 2 show the typical optical photographs of monolithic virgin gel and gel sample containing $NiCl_2$ and glucose after drying.

Therefore, it can be concluded that higher acid content [2·5 c.c. of 8(N) HCl] is a significant factor for the formation of monolithic gel. The ageing time and leaching time do not appear to be that significant.

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