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Study of phase-transfer-catalyst influence in $CaO–SiO_2$ Gel preparation

E. CORDONCILLO, G. MONRÓS, M. A. TENA, P. ESCRIBANO, J. CARDA
E.S.T.y Ciencias Experimentales, Area de Química Inorgánica Universitat Jaume I, Spain

Gels in a $CaO–SiO_2$ (20:80 wt%) system were prepared in a heterogeneous phase. The following phase-transfer catalysts were tested: 18-Crown-6, 15-Crown-5 and tetrabutylammonium hydrogenosulphate. The influences of the polarity of two non-classical solvents (toluene and dichloromethane) were also studied. The degrees of polymerization and of oxide contents were analysed by infrared spectroscopy and thermal analysis. Finally, the morphology and structure of the dry and fired gels were studied by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

1. Introduction

The so-called sol–gel process has been gaining scientific and technological interest during the last few years, leading to new contributions in *glasses-and-ceramics* studies [1, 2].

Preparation of polymerization from the hydrolysis and condensation of alkoxides has been sufficiently studied for SiO_2; data on multicomponent systems, however, is still limited [3].

Different precursors such as organic metal compounds and inorganic metallic salts have great differences in their reactivities. Thus, materials with different homogeneities can be prepared by varying the experimental conditions [4]. Similarly, a less investigated field is that of the sol–gel process, in which multicomponent systems with precursors of different natures take part by using so-called phase-transfer catalysts (PTCs) [5] on one hand, and working with non-classical solvents with different polarities on the other. A diphasic system is formed after the addition of water to toluene and dichloromethane solvents; strong insolubility appears in some precursors with these kinds of solvents. In this sense, data from the literature show that crown ethers are very efficient catalysts in solid–liquid two-phase reactions while ammonium salts are better catalysts in liquid–liquid two-phase systems [6]. In order to avoid the hydrolysis of metallic precursors, the gelification could take place in an organic phase and a higher degree of gel homogeneity could be reached. An ideal PTC action mechanism is shown in Fig. 1.

The preparation of glasses in $CaO–SiO_2$ systems by means of sol–gel processes has scarcely been studied [7, 3]. In order to obtain glasses in these systems, Villegas and Navarro [8] prepared these glasses at lower temperatures than those required to obtain glasses by fusion using the sol–gel technique. They obtained an amorphous glassy material at temperatures over 900 °C, working in an isopropanol solution.

The equilibrium phase diagram in the $CaO–SiO_2$ system shown in Fig. 2 shows a broad area of glass formation (with a high temperature) and a liquid–liquid immiscibility part [9, 10].

The aim of this research was to study gel formation in a $CaO–SiO_2$ system using a PTC in solvents of different nature, monitoring their evolution with thermal treatment and characterizing, by spectroscopy and microscopy techniques, the structure and microstructure of the gels formed.

2. Experimental procedure

2.1. Sol preparation, gelification and thermal treatments

Non-classical solvents were chosen in our research, and experiments were carried out in toluene and dichloromethane. Tetraethoxysilane (TEOS) was used as a silicon precursor (TEOS > 98%, Merck) and calcium acetylacetonate, $Ca(CH_3COCHCOCH_3)_2\ xH_2O$ ($Ca(acac)_2$, Strem Chemicals, Inc), was used as a precursor of CaO; 0.11 M HCl was used as an acid catalyst and three PTCs were tried: 18-Crown-6

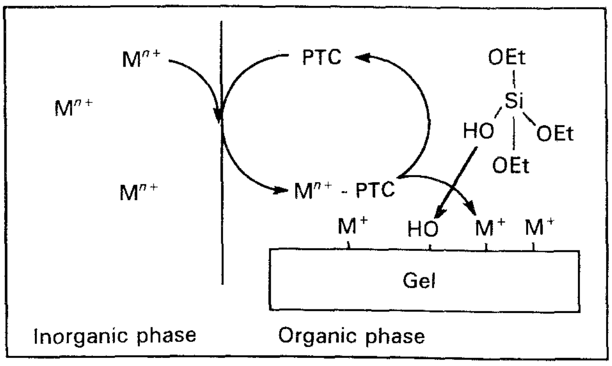

Figure 1 Idealized scheme of PTC mechanism in a heterogeneous phase.

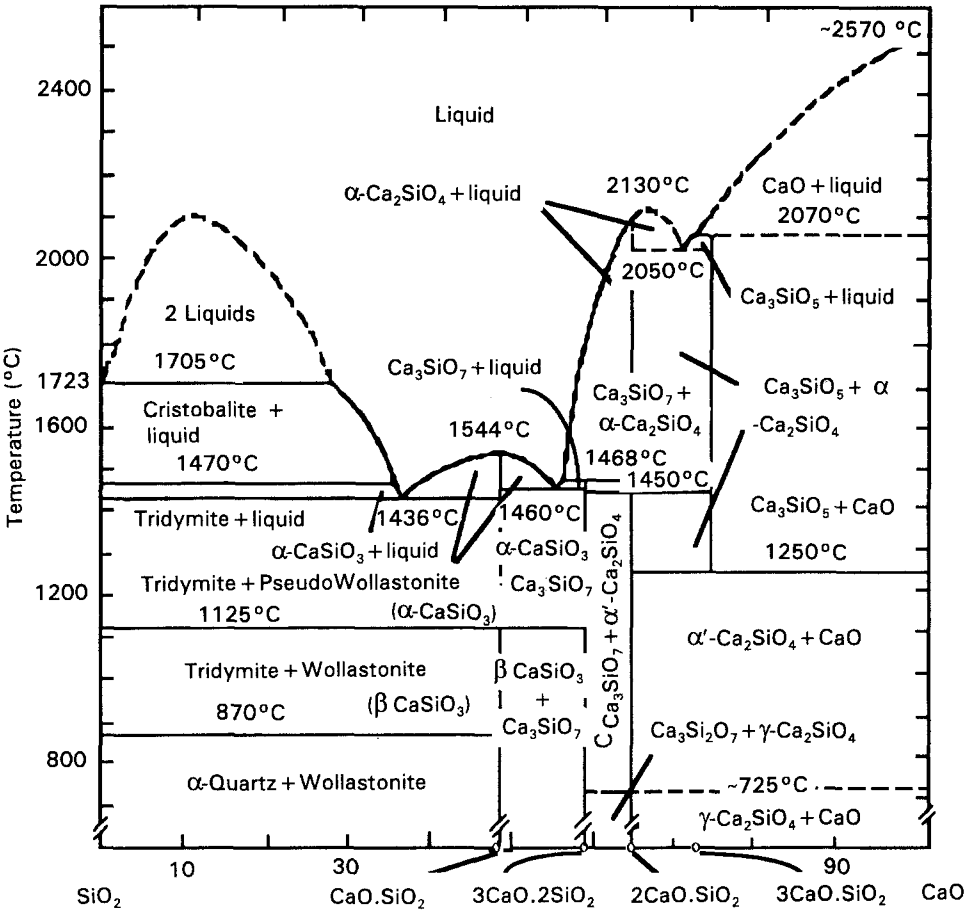

Figure 2 Equilibrium phase diagram in the CaO-SiO_2 system (9, 10).

(18C6 99%, Aldrich), 15-Crown-5 (15C5 98%, Aldrich) and tetrabutylammonium hydrogenosulphate (TBAS > 98%, Merck).

Fig. 3, shows the gel process carried out for glass formation. The TEOS/salt relationship was as required for a final composition of 20:80 (CaO–SiO_2 wt%). The molar ratio of TEOS/H_2O/H^+ and the concentration of PTC were 1:2:0.0036 and 3.6 $\times 10^{-3}$ M, respectively. In all cases 50 ml of solvent was used.

In general, gels were prepared by adding the precursor salts to the solvents in a flask at atmospheric pressure. TEOS and the catalyser were also added to the precursor. Finally, the PTC was added to the mixture. The samples were heated under reflux for two days. Drying were carried out at room temperature by means of an air flow, in order to complete the evaporation of the solvent.

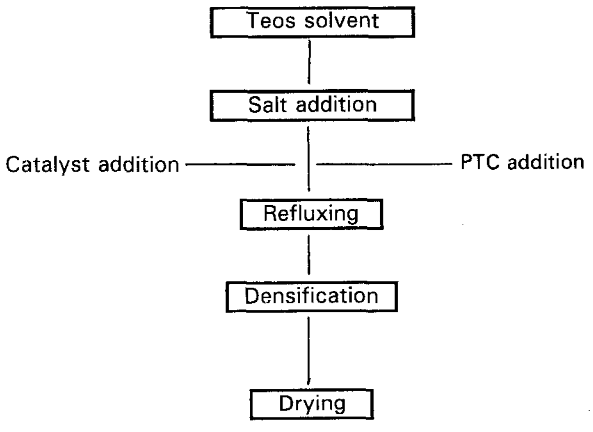

Figure 3 General process carried out in samples preparation.

The samples prepared, classified by the solvent and the PTC used, are given in Table I.

The dried gels were fired in an electrical furnace (Carbolite type HTC 15/8, with a maximum temperature of 1500 °C) under atmospheric pressure. The calcination cycle (Fig. 4) was chosen after the dry gels were studied by differential thermal analysis (DTA) or thermogravimetric analysis (TGA).

2.2. Sample characterization

Infrared (i.r.) spectroscopy (KBr pellets) in the range 4000–201 cm^{-1} was used to study the structural evolution of gels with a Perkin–Elmer spectrophotometer with a 3600 data station, using the standard CDS13 program for data handling.

Dry and fired gels were analysed by X-ray diffraction (XRD) using the powder method, with CuK_α radiation and a Ni filter in the 2–70° (2θ) zone, with a Philips PW-1729 diffractometer.

Differential thermal analysis (DTA) or thermogravimetric analysis (TGA) were performed in the range 50–1100 °C, at 20 °C min^{-1} under an air atmosphere in a Perkin–Elmer high-temperature differential thermal analyser, model DTA 1700, and in a Perkin–Elmer thermogravimetric analyser, model TGA 7, respectively.

TABLE I Sampes prepared with precursor, solvent and PTC relationship.

	TOLUENE				DICHLOROMETANE			
PTC	-------	18 C 6	15 C 5	TABS	-------	18 C 6	15 C 5	TBAS
Ca(acac)$_2$	m1	m2	m3	m4	m5	m6	m7	m8

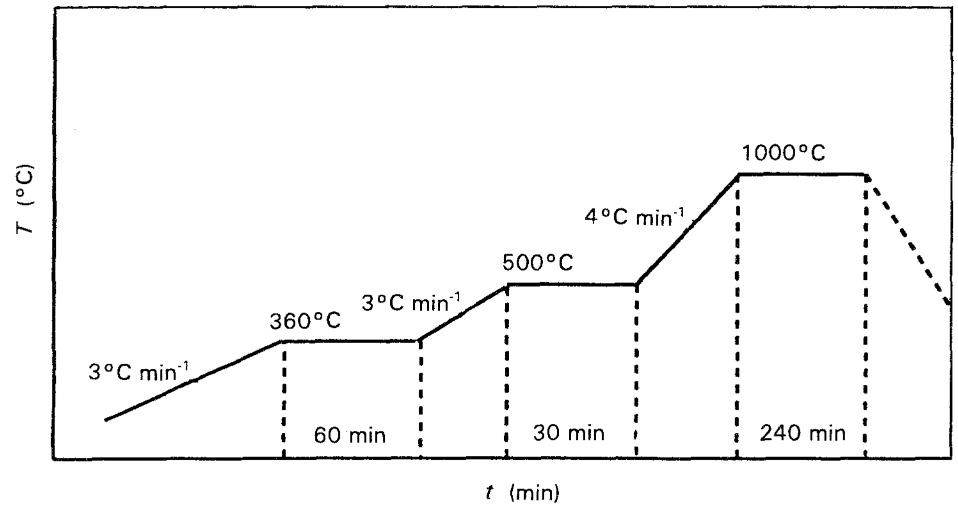

Figure 4 Calcination cycle used in the thermal treatments.

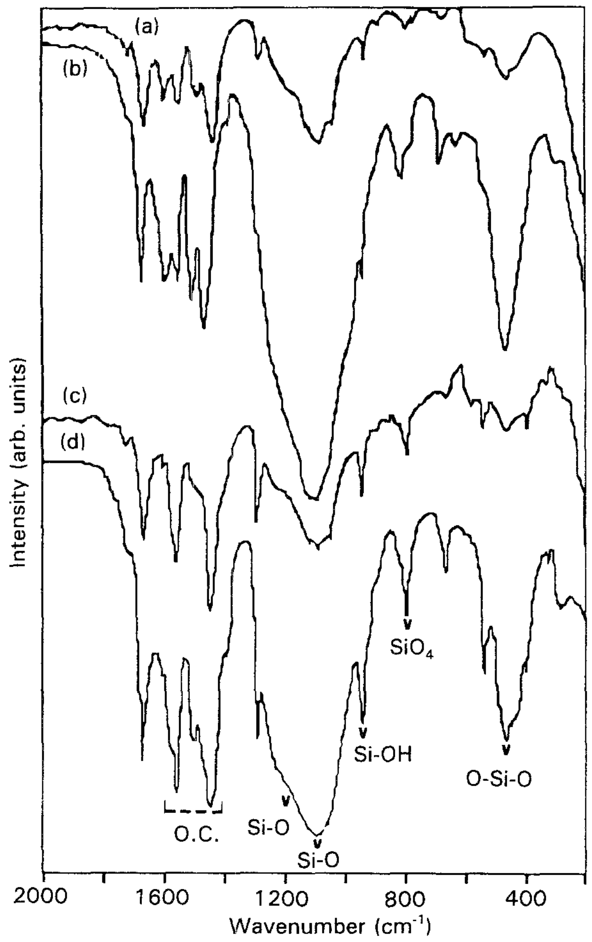

Figure 5 IR spectra of samples prepared in toluene as solvent. Samples: (a) m1, (b) m2, (c) m3, (d) m4. O.C.: organic compounds.

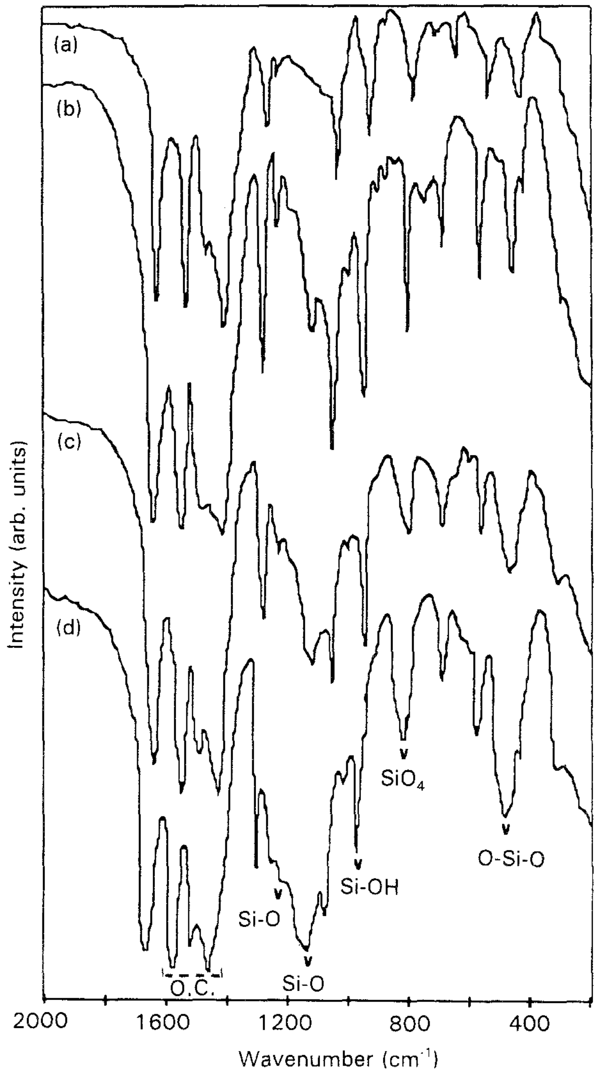

Figure 6 IR spectra of samples prepared in dichloromethane. Samples: (a) m5, (b) m6, (c) m7, (d) m8.

The study of dried and fired gel textures was followed by scanning electron microscopy (SEM), with a Hitachi S-2500 electron microscopy.

3. Results and discussion

3.1. I.r. band study

The i.r. spectrum of all the samples showed the characteristic bands assigned to C–H bending at 1333 cm^{-1} [11]. Weak bands in the range 1600–1380 cm^{-1}, assigned to organic peaks of acetylacetonate, were also observed. A shoulder around 1200 cm^{-1} appeared in all spectra; it was attributed to asymmetric stretching of Si–O.

When the 18C6 was used as a PTC, the peaks at 1090 cm^{-1} (asymmetric bending of Si–O) and at 468 cm^{-1} (bending of O–Si–O) were bigger than without PTC [12]; furthermore, with this PTC, the Si–OH band at 952 cm^{-1} showed the best resolution and the highest intensity [13].

In all cases, an increase in resolution of the SiO_4 band at 800 cm^{-1} was observed with the use of all PTCs [11]. However, the presence of a peak of the acetylacetonate in the same region could produce a mistake. Fig. 5 shows the i.r. spectra for the toluene samples.

The i.r. results obtained with the other solvent (CH_2Cl_2) seemed to have a less effective band resolution. Samples were synthesized with good polymeric bands as can be seen in Fig. 6.

These results showed that the role of a PTC in the toluence solution was very positive in SiO_2–CaO polymeric network formation, and that the 18 C 6 was the most effective at network building.

3.2. XRD and DTA–TGA study

The results of the XRD analysis of the dried and fired gels are shown in Table II. As can be seen from Table II, amorphous dry gels were obtained with the samples in toluene and with 18C6 or 15C5 as PTC, and the rest of the samples showed peaks of the precursor salts; these results could indicate that these PTCs transported the salts from the inorganic phase to the gel phase.

In fired gels, amorphous powder appeared in the samples prepared with toluene and 18C6 or TBAS as the PTC. When dichloromethane was used as a solvent, the TBAS addition led to an amorphous material. In the other samples, a medium or small crystallization of calcium silicates ($CaSiO_3$ or Ca_3SiO_5) was detected.

Fig. 7 shows selected DTA–TGA diagrams of the most representative samples (m2 and m8) for the two solvents studied. The oxide contents calculated from the TGA analysis (Table III) indicated that the highest oxide content was in sample m2 (prepared with 18 C6 and toluene). The other PTC was less effective for this parameter.

In all samples prepared in a dichloromethane solution, stabilization of the TGA curve was observed at temperatures over 800 °C; and, can be seen in Fig. 7, sample m8 showed the highest oxide content, but this oxide content was clearly smaller than in the same sample with toluene as the solvent. These results were consistent with the development of characteristic polymeric bands observed in i.r. spectra.

Generally, three regions of weight loss were present in the TGA of all the samples. The first was due to water and occluded solvent evaporation (a DTA endothermic peak) in the 60–120 °C range. The second

TABLE II Results of the XRD analysis of dried and fired samples.

sample	m1	m2	m3	m4	m5	m6	m7	m8
XRD dry	S(vw)	am	am	S(m)	S(s)	S(s)	S(vw)	S(vw)
XRD fired	C(m)	am	A(W)	am	A(m)	A(m)	C(m)	am

a = α-$CaSiO_3$; C = Ca_3SiO_5; S = salt precursor; am = amorphous.
Peaks intensity; vw = very weak; m = medium; s = strong.

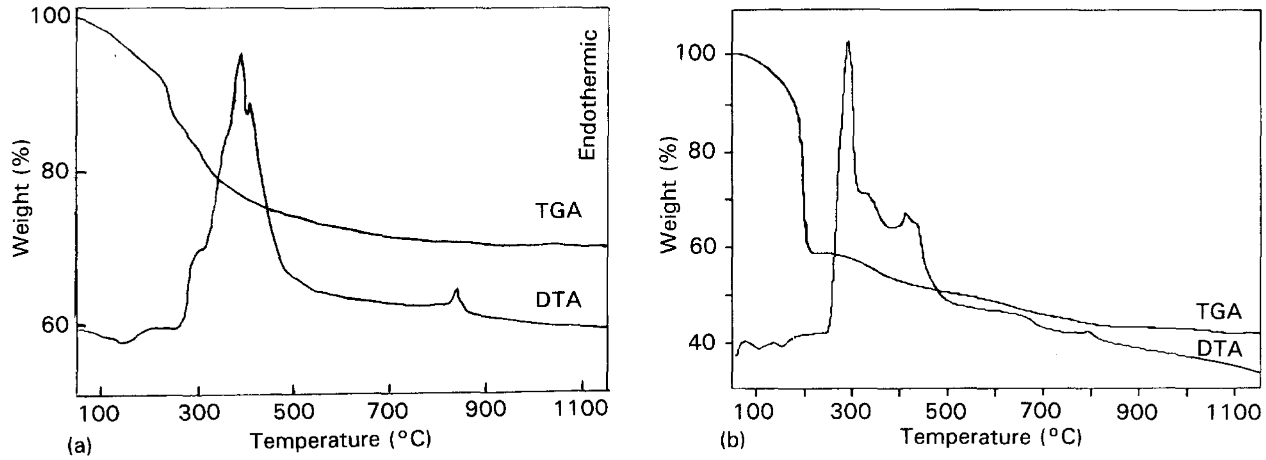

Figure 7 (a) DTA-TG diagrammes of the m2 sample. (b) DTA-TG diagrammes of the m8 sample.

TABLE III % oxide content obtained from TG analysis.

sample	Oxide content (wt %)	sample	Oxide content (wt %)
m1	65	m5	32
m2	70	m6	33
m3	50	m7	35
m4	64	m8	46

TABLE IV Relation of loss weight (Δ%) in the 460 to 760 °C range taking sample m2 as reference.

sample	Δ%(m)/Δ%(m2)	sample	Δ%(m)/Δ%(m2)
m1	1.4	m5	3.6
m2	1.0	m6	4.8
m3	2.9	m7	3.0
m4	1.5	m8	2.3

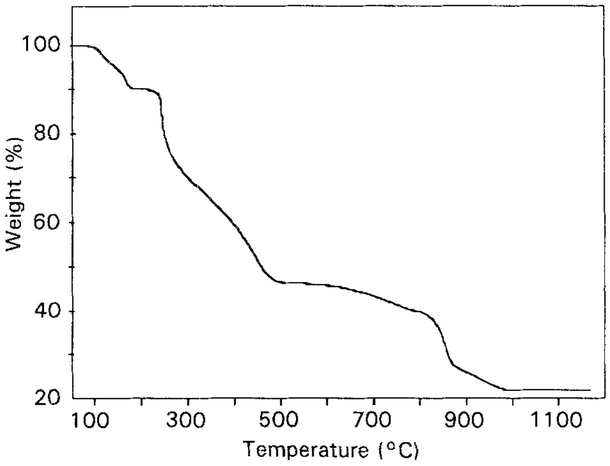

Figure 8 TG diagram of $Ca(acac)_2$ as salt precursor.

was assigned to an organic-group combustion (a DTA exothermic peak), in the 240–500 °C range, and the third region, in the range 460–760 °C, did not coincide with the oxidation of not hydrolysed organic TEOS groups. This loss of weight was probably due to the combustion of organic groups of the $Ca(acac)_2$; the salt precursor was not included in the gel network, as can be observed in Fig. 8 of the $Ca(acac)_2$. This fact could indicate a homogeneity in the degree of gel forming. In this sense, there could be a relationship between the intensity of this weight loss and the presence of a crystalline phase in the raw gel. The relations of weight loss in the range 460–760 °C, for TGA using sample m2 as a reference, are shown in Table IV. This sample presented an amorphous phase in the dry gel (Table II) and the best oxide contents (Table III).

The little exothermic peak that appeared in the DTA plots around 900 °C was due to crystallization, and it can be observed by XRD (summarized in Table II). In the case of sample 4 (with TBAS as the PTC), this peak appeared below 850 °C.

3.3. Morphology study by SEM

The observation of the texture of the dry gels by SEM (Fig. 9) indicated that in the case of the gels without a PTC (m5 sample) the sample was heterogeneous (Fig. 9a) with large crystals, which were assigned to the salt precursor by XRD, and it had small particles deposited on these crystals. In the case of the samples with 18 C 6 as the PTC and with toluene as the solvent (m2), crystallizations were not observed and the morphological aspect was homogeneous, with very large

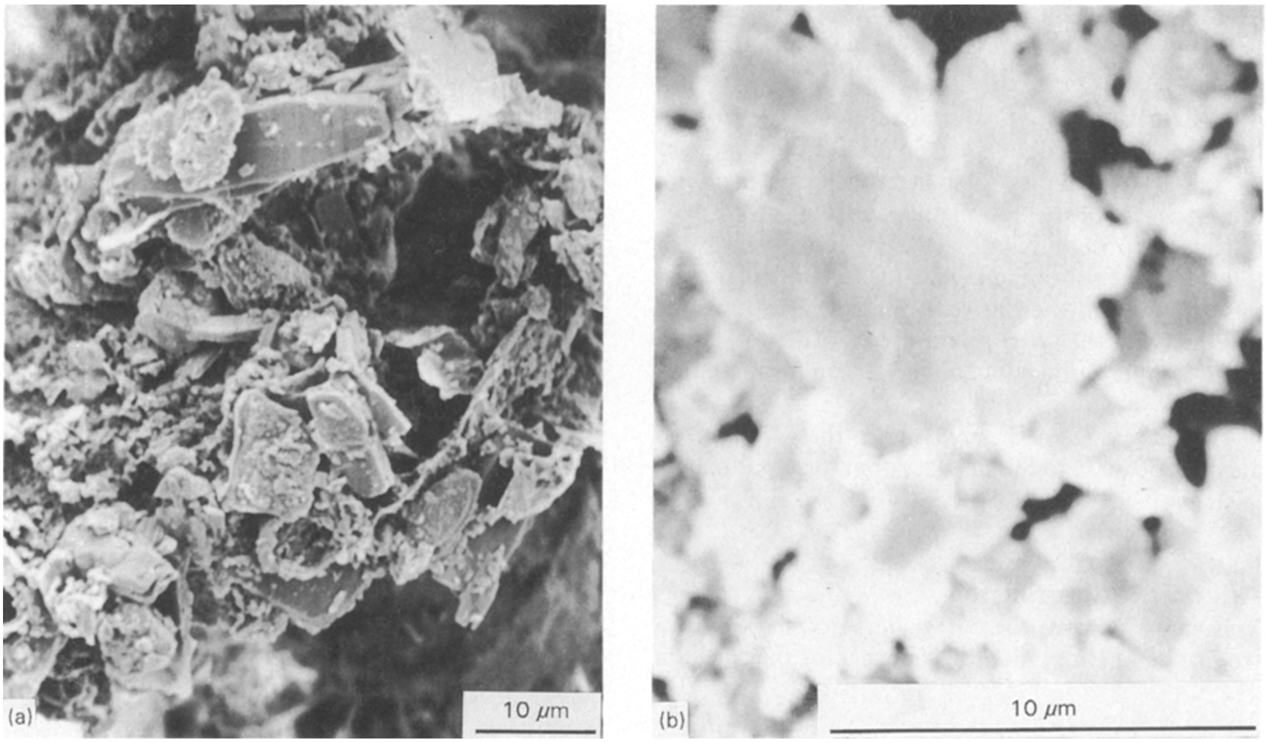

Figure 9 SEM micrograph of representative samples: (a) m5 sample, × 1500 magnification; (b) m2 sample, × 3000 magnification; (c) m8 sample, × 2200 magnification and (d) m4 sample, × 2000 magnification.

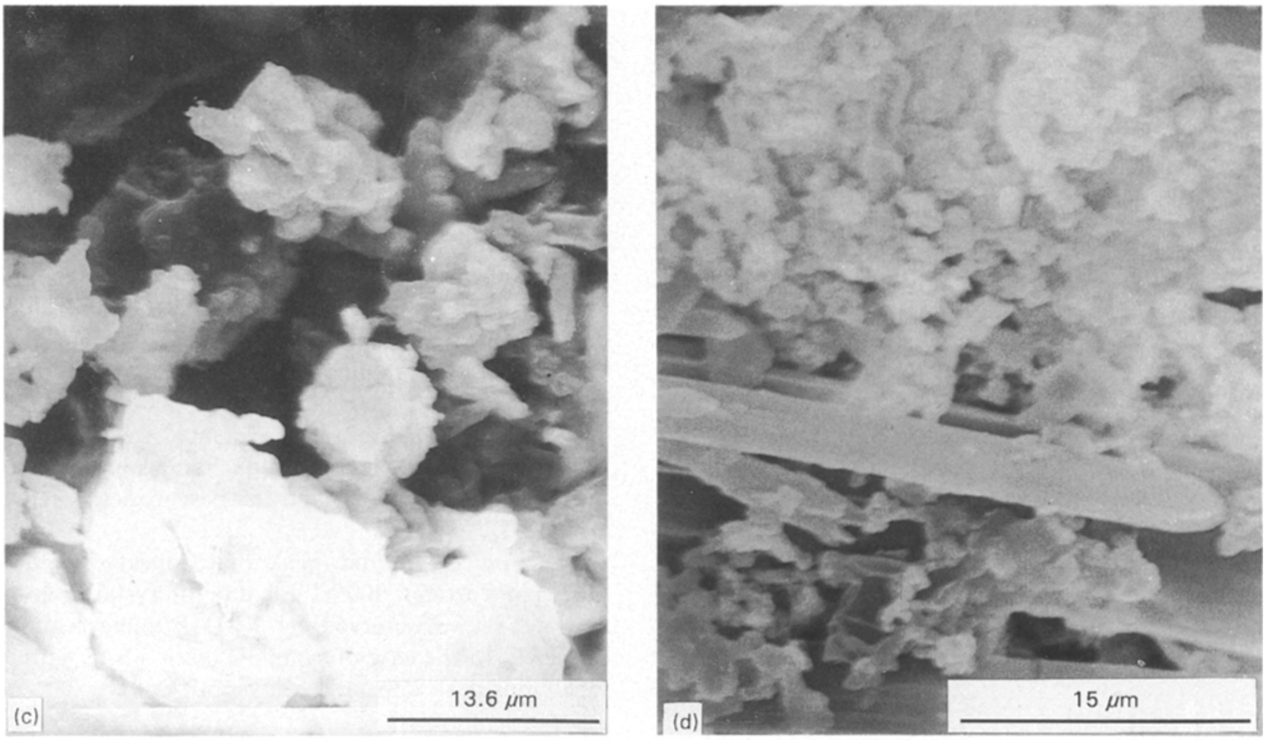

Figure 9 (continued)

blocks with an average size of 10 μm (Fig. 9b). However, crystals were present in these samples when dichloromethane was the solvent, confirming the presence of the salt precursor observed by XRD. Similar results were obtained in the samples with 15 C 5 as the PTC (samples m3 and m7). Finally, homogeneous blocks were observed in the gels obtained with TBAS as the PTC and with dichloromethane as the solvent (sample, m4, Fig. 9c). In the case of the same samples prepared with toluene, large crystals were observed (Fig. 9d).

4. Conclusion

It was possible to obtain gels in a $CaO–SiO_2$ system by sol–gel techniques in a heterogeneous medium, using toluene or dichloromethane as the solvent.

The best results in the gellation range were with toluene as the solvent and with 18 C 6. The polarity of this solvent and the different refluxing temperatures together with the appropriate size of 18 C 6 for cation Ca^{2+} complexation could be the reason for this efficiency.

The materials synthesized under these conditions may be adequate to obtain glass or amorphous materials.

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