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A DSC study of the drying process of TEOS derived wet silica gels

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Abstract

The drying process of wet silica gels obtained from TEOS has been studied by means of FT–IR, DSC and specific surface area measurements. FT–IR spectroscopic results have not given any important information about the drying process of silica gels. However, DSC results have shown a dependence of the DSC peak area on drying time. Three different water/alkoxide ratio were studied, and the DSC peak area was higher when the water/alkoxide ratio increased. A more open xerogel structure was found for the high water/alkoxide ratio showing a high specific surface area and therefore lower drying times. For the silica gels obtained with 200/1 and 100/1 water/alkoxide molar ratio, a complete drying time was observed for 25 and 28 days, respectively. As the drying time increases the gel structure becomes more closed, being necessary higher temperatures for removing water or alcohol from the gel. © 1997 Elsevier Science B.V.

Keywords: Sol–gel; Silica; Drying; DSC; FT–IR

1. Introduction

It is well known that the sol–gel method is widely applied in the synthesis of glasses, glass-ceramics and ceramic materials. This method is based on the hydrolysis and polycondensation reactions between metal alkoxides and H_2O in presence of a solvent [1]. Alcohols (ethanol, propanol, isopropanol, etc.) are generally used as solvents. In general, the sol–gel process can be viewed as a sequence of inter-related subprocesses which involve firstly the mixing of liquids, the gelling of the liquid mixture, the removal of residual organics and water from the porous solid gel by heat treatment at low temperature and finally the densification of the dried gel by a heat treatment at high temperature to obtain a monolithic dense material. During the hydrolysis reaction, the metal alkoxide reacts with H_2O and therefore new alcohol molecules appear and M–OH (M = Si, Al, Ti, Zr, etc.) groups are formed. During the polycondensation reactions the M–OH groups react forming M–O–M bonds plus H_2O. As polycondensation increases the sol is transformed into a gel of continuously increasing viscosity. Although alcohols and H_2O are exuded from the gel during polycondensation, a large part of these compounds are retained in both open or close pores of the gel. This wet gel is then heat treated at low temperature during the drying step in order to eliminate as much as possible H_2O and alcohols from it. It is now recognized that the gel-to-glass conversion is very dependent on the physical and chemical properties

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of the dried gels. The presence of pores with different sizes and also OH groups in the dried gel give a recognized difficulty in preparing massive glasses because of both fracture and bloating during firing. Therefore long drying times are needed because the small pores create large capillary forces [2] which tend to fracture the gel during firing.

On the other hand, the collapse of pores during firing avoid the removal of residual organic compounds and water from the gel. Therefore, it is necessary to eliminate the residual compounds completely before closing of any pores.

It has been shown that long drying times give dried gels of lower bulk density and higher surface area and pore volume with a wider pore size distributions than gels dried for shorter times [3]. These low density gels are transformed to glass without fracture or bloating.

Since the drying process of wet gels is a fundamental step for obtaining a non-broken and non-bloating glasses, specific surface area are measured in this work, we have studied this step by means of infrared spectroscopy and differential scanning calorimetry (DSC). We show here that DSC is an appropriate technique for studying the evolution of the drying process in wet gels.

2. Experimental

2.1. Sample preparation

Silica xerogels were prepared by thoroughly mixing two solutions at 50°C. The first solution contains tetraethoxysilane (TEOS) and ethanol and the other solution contains H_2O, ethanol and HCl. Three molar ratios were investigated, these were 200/1/4/0.1, 100/1/4/0.1 and 25/1/4/0.1 (H_2O/TEOS/ethanol/HCl). The total volume of ethanol was divided between both solutions. In the three reactions the total volume of the solution was 200 cm^3. These reactions were carried out in a 500 ml beaker coupled with a reflux condenser, a mechanical stirrer and an additional burette. Firstly, the TEOS/ethanol solution was added to the beaker and the H_2O/ethanol/HCl solution was later drop-wise added under vigorous stirring. The whole solutions were stirred for one day and then were poured into glass containers then they were covered with plastic film and maintained at 50°C in an oven at room temperature. The gelation of these solutions occurred within 48 h. After gelation, the wet gels were dried in the same oven at 50°C. The glass containers, where gel was inside, were only opened for taking out samples for DSC and infrared characterization.

2.2. Experimental techniques

Differential scanning calorimetry measurements were carried out in a DSC-7 (Perkin–Elmer) equipment. Gel samples of about 30 mg were placed inside the closed aluminum containers. The measurements were carried out at 10°C min^{-1} in a dry nitrogen (0,9999 purity) atmosphere. The DSC-7 equipment was previously calibrated.

The infrared spectra of the gels were measured in a 1760 X (Perkin–Elmer) Fourier Transform–Infrared Spectrophotometer (FT–IR) in the 4000–400 cm^{-1} spectral range with a resolution of 4 cm^{-1}. Ten scans were measured for each spectrum. The KBr pellet method was used where 1 mg of gel sample and 300 mg of KBr were mixed thoroughly and quickly and then pressed at 8 tons for 2 min under vacuum.

Specific surface areas of the dried silica gels were measured in a home-made apparatus [4] using nitrogen as adsorbate. The silica xerogel was firstly degassed at 50°C for 18 h in a dry He stream. The measurements were carried out at 77 K. Specific surface areas were obtained using the BET equation [5] at a partial pressure of 0.35 and assuming 0.162 nm^2 as the area of the nitrogen molecule.

3. Results

Figs. 1–3 show the FT–IR spectra of the wet silica gels dried at different time interval at 50°C. These spectra show the same IR bands irrespective of drying time. The OH stretching vibrations take place in the 3000–4000 cm^{-1} region and at 1630 cm^{-1} the band corresponds to OH bending. In all these spectra the bands are observed at 1170, 1080, 800 and 460 cm^{-1} corresponding to Si–O–Si bonds of the silica gel [6–8]. The peaks appearing at 960 and 550 cm^{-1} are associated with Si–OH and siloxane backbone vibrations, respectively [9]. All of these peaks appear in the same position independent of both molar ratio of starting solutions and drying time. These spectra were

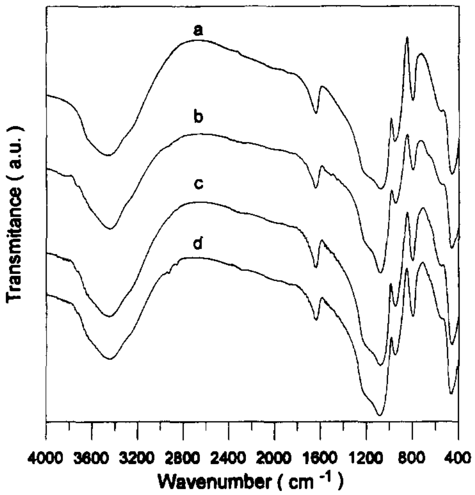

Fig. 1. Infrared spectra of wet silica gels of 200/1 (H_2O/TEOS) molar ratio at different drying times: (a) 6; (b) 16; (c) 21; and (d) 25 days.

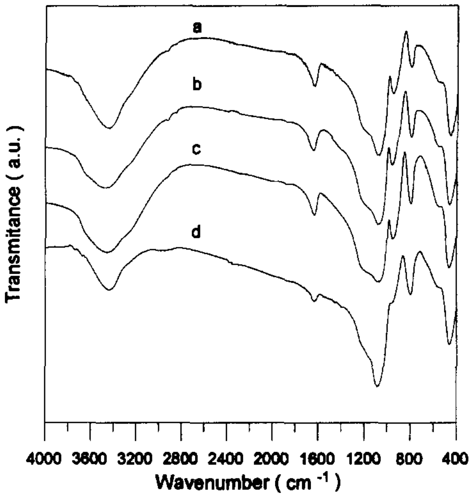

Fig. 3. Infrared spectra of wet silica gels of 25/1 (H_2O/TEOS) molar ratio at different drying times: (a) 5; (b) 15; (c) 25; and (d) 30 days.

changed to absorbance units and the area of each IR peak was obtained by a deconvolution procedure assuming a gaussian profile for the IR peak. The area of each peak should be related to the concentration of the chemical bond which gives the IR peak. However, when we plot the peak area as a function of drying time or water/alkoxide ratio we do not find any correlation. This result has also been observed for silica xerogels obtained for lower H_2O/TEOS ratios [10] and has been assigned to the process of preparing the KBr pellet for IR measurements. H_2O and alcohols retained inside the gel are removed during mixing with KBr and also with the later vacuum process for obtaining the IR pellet, and their concentration may not be followed by FT–IR measurements. In view of this result, we have used the DSC technique because a small sample is put inside a container without handling further. Since the removing of water and alcohol is carried out from bulk to the surface of the gel piece, we have always used a sample obtained in the same region of the gel piece. However, some dispersion of the experimental data has been obtained, as it is observed in the following figures.

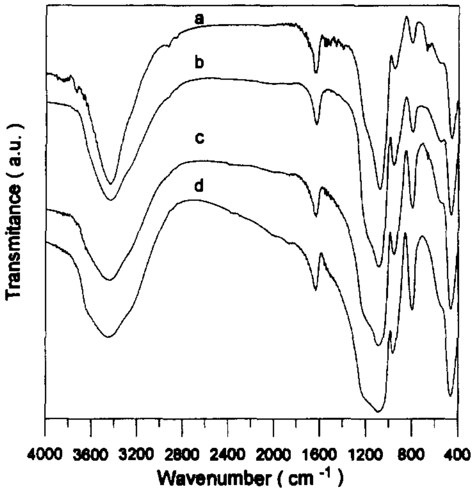

Fig. 2. Infrared spectra of wet silica gels of 100/1 (H_2O/TEOS) molar ratio at different drying times: (a) 4; (b) 15; (c) 26; and (d) 28 days.

Figs. 4–6 show the DSC curves of the wet silica gels for different drying times. The observed endothermic peaks are due to removal of H_2O and alcohol (ethanol) adsorbed or occluded (condensed) in pores of the gel. However, part of this H_2O is due to the dehydration polymerization process taking place when temperature is increased during the measurement. It is clearly observed that the DSC peaks decrease in width and intensity when drying time increases. At the same time the temperature of the maximum of the DSC peak increases. These results confirm the possibility of studying the drying step of the sol–gel process by DSC analysis.

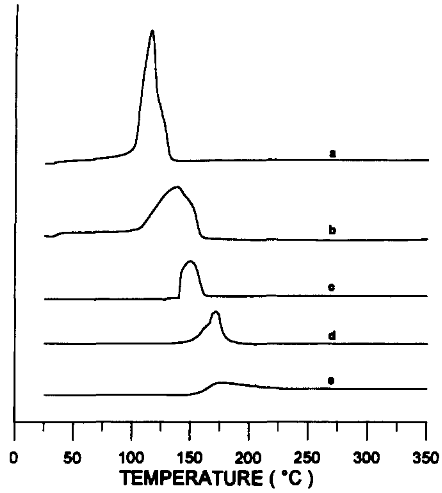

Fig. 4. DSC measured curves for wet silica gels of 200/1 (H_2O/TEOS) molar ratio at different drying times: (a) 4; (b) 8; (c) 16; (d) 21; and (e) 23 days.

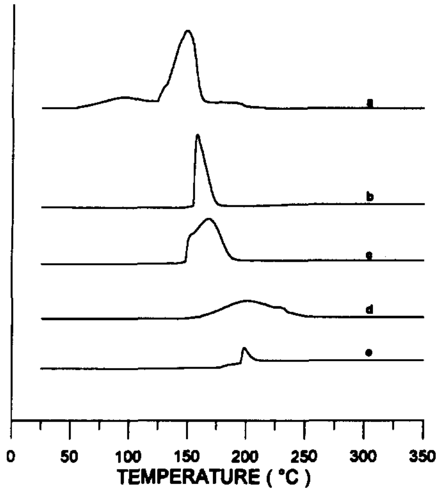

Fig. 6. DSC measured curves for wet silica gels of 25/1 (H_2O/TEOS) molar ratio at different drying times: (a) 3; (b) 8; (c) 18; (d) 25; and (e) 28 days.

4. Discussion

Since FT–IR spectroscopic results have not given any information about the drying process of silica gels, we have focused our study to the DSC results.

The high H_2O/TEOS ratios employed in this work have been chosen in order to obtain completely hydrolysed gels, where any etoxy groups are present. Shukla and Johari [11] showed that for molar ratios H_2O/TEOS of 15/1 the TEOS hydrolysed was about 93%. Then the area of the DSC peak must correspond to the whole H_2O and alcohol removed from the silica xerogel during the measurement. These compounds are those that have not been removed during drying in the oven at 50°C. Therefore, measuring the area of the DSC peak and subtracting the base line we can quantify the drying process. The results obtained for the three silica gels are shown in Fig. 7. It is observed in this figure that on the first day of drying the area of the DSC peaks are higher when H_2O/TEOS ratio is increased. This result shows that the gel maintains in its structure a great part of H_2O and alcohol employed for the reaction.

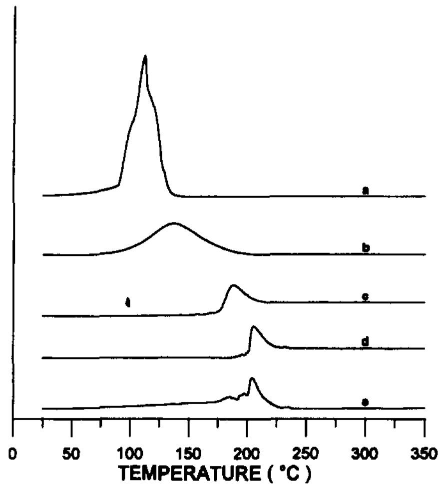

Fig. 5. DSC measured curves for wet silica gels of 100/1 (H_2O/TEOS) molar ratio at different drying times: (a) 2; (b) 10; (c) 20; (d) 24; and (e) 26 days.

On increasing the drying time, two steps are observed in the curves of Fig. 7. The first step occurs at a lower drying times for the low H_2O/TEOS molar ratio. This result shows that the polymerization process that occurs during drying is favoured to low H_2O/TEOS ratios. The H_2O molecules must be bounded to OH groups by hydrogen bonding and retard the polymerization between adjacent Si–OH groups. In Fig. 7, we can see that the final area of this first step is higher for the low H_2O/TEOS ratio. This result shows that the microtexture of the gels is dependent on the H_2O/TEOS ratio. A high opened pore structure where H_2O and alcohol may be easily removed can be assigned to

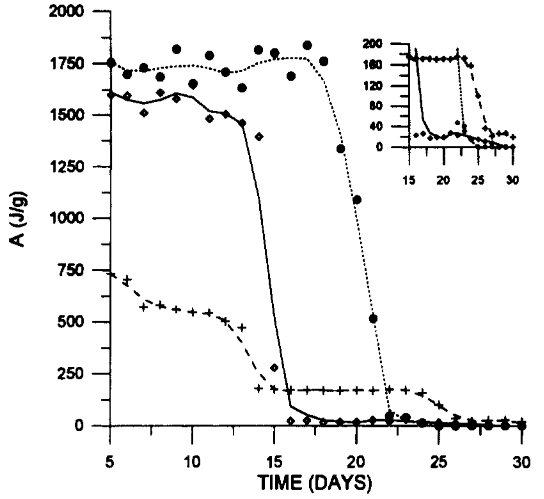

Fig. 7. Variation of the DSC peak area as function of drying time of wet silica gels obtained at different H_2O/TEOS molar ratios: ● 200/1; ◇ 100/1; and + 25/1.

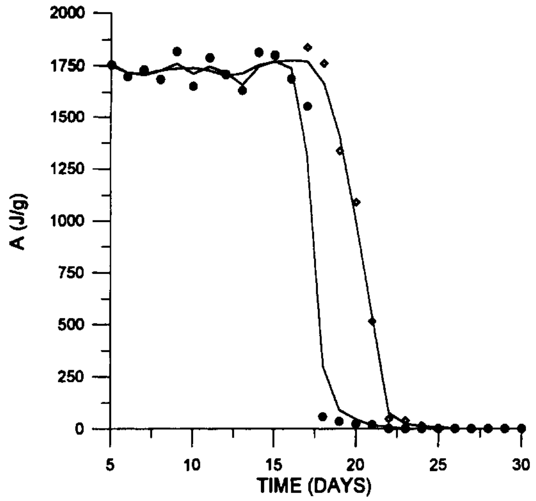

Fig. 8. Variation of the DSC peak area as function of drying time of wet silica gels dryed at different temperatures: ● 50, 80 and 120°C, ◇ 50 and 120°C.

gels of high H_2O/TEOS ratio. This behaviour is maintained till the end of drying.

In order to verify this later assignment, the specific surface areas (SSA) were determined by the adsorption of nitrogen on the silica xerogels dried for 30 days. The SSA values were 710, 583 and 473 $m^2 g^{-1}$ for xerogels obtained for H_2O/TEOS molar ratios of 200/1, 100/1 and 25/1, respectively. These values show a high open pore structure for the higher H_2O/TEOS ratio which confirms DSC results. Using the percolation theory for adsorption–desorption nitrogen isotherms, we have found that the pore structure has similar pore interconnection for the three xerogels [12]. This interconnection between pores and the high surface area gives a higher possibility of removal of H_2O and ethanol and then a low concentration of such compounds must remain in the xerogel dried for long drying times, as it is observed in Fig. 7.

As we have mentioned before, the drying schedule of a wet gel influences its final properties. For silica gels different drying temperatures have been used in the literature [1,7,10,13]. Now we have studied, by DSC, the effect of a different schedule for drying wet silica gels. In this new schedule the wet silica gel of H_2O/TEOS = 200/1 molar ratio was dried at 50°C for two weeks and then heated at 80°C for one week and at 120°C for another one. The obtained results are compared in Fig. 8 with those of the same wet silica gel dried at 50°C for 25 days and then at 120°C. In both cases a heating rate of 10°C/min was used. The results of Fig. 8 show the same behaviour for both drying schedules. However, the silica gel dried at high temperature shows a decrease of the DSC peak area for shorter times. This is consistent with a high rate of evaporation of H_2O and ethanol at higher temperatures. When both gels were dried at 120°C no DSC peak was observed and thus we can conclude that such gels are completely dried (xerogel).

It is well known that ethanol and molecular water physically adsorbed onto the surface of silica can be removed by evacuation even at room temperature [14], whereas vicinal and geminal hydroxyl groups are removed only by heating. Hydrogen bonded surface silanols codense and eliminate water at approximately 170°C [14,15]. The results obtained in this work are in accordance with such condensation of silanols.

The results of Figs. 4–6 show the decrease of the peak area and also the increase of the peak temperature upon heating. Fig. 9 shows such change in peak temperature with drying time. The increase of the peak temperature can be resulted from both less concentration of hydrogen bonded silanols when the drying time was increased or higher difficulty of removing water and ethanol by the continuously gel contraction.

In all cases the peak temperature is higher than the one corresponding to H_2O evaporation showing a

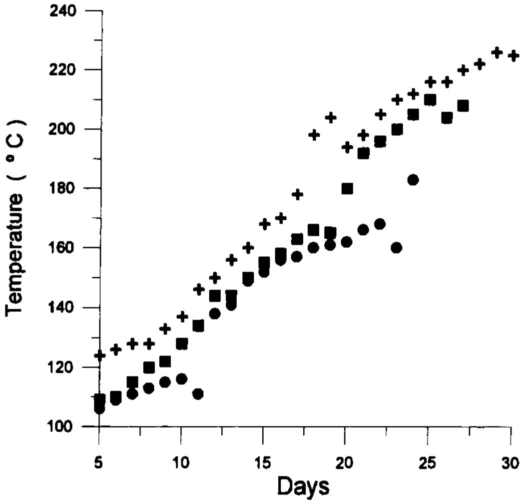

Fig. 9. Variation of the DSC peak temperature with drying time for wet silica gels of different H_2O/TEOS molar ratios: ● 200/1; ■ 100/1; and + 25/1.

strong interaction between water molecules and silanol groups of the wet silica gel, and also the presence of such compounds in open or close pores of the gel. Fig. 9 shows an inverse dependence of the peak temperature on the H_2O /TEOS ratio. Therefore, the silica gel which has been obtained with high H_2O concentration has a more open structure from which H_2O and alcohol can be more easily removed. This result is in accordance with the above mentioned high-specific surface area. An open structure will give both high specific surface area and low temperatures for removing water and ethanol from it.

It can be observed in Figs. 7 and 9 that for a given peak temperature the area of the peak is different for each gel and this effect is due to a different structure (opened/closed) depending on the H_2O/TEOS ratio used for hydrolysis.

5. Conclusions

This study has shown the importance of using the DSC technique in studying the drying process of wet silica gels obtained from TEOS. By analysing temperature and peak areas of DSC curves it was possible to follow the water and alcohol content in the gel for each drying time. It has been observed that on increasing the H_2O/TEOS ratio a more open gel structure is obtained, where water and alcohol can be removed more quickly and at low temperatures than for lower H_2O/TEOS ratios.

The drying schedule was also studied by DSC. As expected, on increasing the drying temperature, the drying time decreases.

Acknowledgements

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References

[1] B.E. Yoldas, J. Mat. Sci. 12 (1977) 1203.
[2] T. Zarzycki, M. Prassas, J. Phalippou, J. Mat. Sci. 17 (1982) 3371.
[3] T. Kawaguchi, M. Hishikura, T. Ioura, Y. Kokubu, International Work show an Glasses and Glass Ceramics from Gels. Wurzberg Germany, July 1-2, 1983.
[4] J.C. Diez-Masa, Chromatographia.
[5] S. Brunauer, P.H. Emmett, E. Teller, J. Am. Chem. Soc. 60 (1938) 309.
[6] A. Bertoluzza, C. Faguano, M.A. Morelli, J. Non-Cryst. Solids 48 (1982) 117.
[7] P. Chu, D.E. Clark, Spectroscopy Lett. 25(2) (1992) 201.
[8] M.C. Matos, L.M. Ilharco, R.M. Almeida, J. Non-Cryst. Solids 147-148 (1992) 232.
[9] H. Yoshino, K. Kamiya, H. Nasu, J. Non-Cryst. Solids 126 (1990) 68.
[10] J. Limpo, J. Rubio, J.L. Oteo, Proc. 3rd European Ceramic Society Congress, Vol. 1, P. Duran, J.F. Fernandez (Eds.), Faenza Editrice Iberica S.L Edit, p. 399.
[11] B.S. Shukla, G.P. Johari, J. Non-Cryst Solids 101 (1988) 263.
[12] F. Rubio, J. Rubio, J.L. Oteo, J. Sol–Gel Sci. Tech., accepted for publication.
[13] L.C. Klein, G.T. Garvey, J. Non-Cryst. Solids 48 (1982) 97.
[14] K.R. Lange, J. Colloid Sci. 20 (1965) 231.
[15] G.T. Young, J. Colloid Sci. 13 (1958) 67.