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## Analysis by DSC of the drying and sintering processes of alkoxide-derived $\text{SiO}_2\text{--ZrO}_2$ gels

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### Abstract

The drying and sintering processes of  $\text{SiO}_2\text{--ZrO}_2$  alkoxide-derived gels have been studied by means of DSC technique. In the drying process, most part of water and alcohols are removed from the gels. For the  $\text{SiO}_2$  gel such elimination occurs at the end of the drying process, however for the  $\text{ZrO}_2$  gel this elimination occurs during the whole drying time. An intermediate behavior is observed for the binary system  $\text{SiO}_2\text{--ZrO}_2$  gels. In the sintering process, the DSC technique allows to determine the elimination of water and alcohols retained within the structure (open or close pores) and the well-known hydroxyl condensation of silica gel between 700° and 800°C is also observed. The  $\text{ZrO}_2$  gel shows the final hydroxyl condensation at the heating temperature of 600°C. For the binary  $\text{SiO}_2\text{--ZrO}_2$  gels, the hydroxyl condensation has been associated to the activation energy needed for the dissociation of silica hydroxyls. This energy decreases with the  $\text{ZrO}_2$  concentration in the gel resulting in a sintering treatment of 500°C leading to the entire hydroxyl condensation for the gel with 75%  $\text{ZrO}_2\text{--}25\%$   $\text{SiO}_2$ .

By studying the temperature of the DSC peaks, it is possible to know the temperature at which most part of water and alcohols are leaving the gel, and these results can be used in order to select the corresponding drying or sintering schedules for obtaining a well-fabricated material. © 1998 Elsevier Science B.V.

*Keywords:* Alkoxide; Drying; DSC; Gels; Sintering;  $\text{SiO}_2$ ;  $\text{ZrO}_2$

### 1. Introduction

In a previous work [1], we have shown that differential scanning calorimetry (DSC) is an useful technique in order to study the drying process of TEOS-derived silica gels. It is possible to study such drying process only by weight loss measurements; however more information can be achieved by DSC analysis. This is because the drying of any alkoxide-derived gels involves the elimination of alcohols and water from the gel network in a simultaneously network

shrinkage. The sol–gel method involves firstly the mixing of liquids, the gelling of the liquid mixture, the removal of residual organics and water from the porous solid gel, and finally a heat treatment at high temperature in order to yield the final material. It is well-known that the different experimental variables selected for each process of the sol–gel method, such as concentration of starting materials, time and temperature of the reaction etc., have a marked influence in the properties of the final material [2]. Different techniques have been used for studying the sol–gel method, these include Fourier-Transform Infrared Spectroscopy (FT–IR), DTA, DTG, XRD, NMR, TEM, etc. These techniques have been basically used

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in the study of the hydrolysis–polycondensation reactions during the gelling of the liquid mixtures [3–6] and in the sintering process during gel-to-final material transformation [7–11]. However, the drying process for obtaining a dried gel (referred as xerogel) from a wet gel has been rarely studied [1]. In this work, we show the results obtained by using the DSC techniques for studying the drying and sintering processes of  $\text{SiO}_2$ – $\text{ZrO}_2$  gels obtained from metal alkoxides.

## 2. Experimental

Gels were prepared from silicon and zirconium alkoxides, alcohols and water. Tetraethylortosilicate (TEOS), Merck for synthesis, was used as source of  $\text{SiO}_2$ , and Zirconium (IV) propoxide (ZP), Fluka for synthesis, as source of  $\text{ZrO}_2$ . Ethanol and *n*-propanol (Merck for analysis) and doubled distilled deionized water were also used in the reactions. The sample preparation involved the dropwise addition of a water/ethanol/propanol mixture to an alkoxide/ethanol/propanol solution, being both solutions previously mixed independently under vigorous stirring. The molar ratio water/alkoxide/alcohol employed were 4/1/1 in all cases. No catalysts ( $\text{HCl}$ ,  $\text{NH}_4\text{OH}$ , etc.) were used in the experiments. The pH of the resulting solution was that provided by the reactants. Five compositions were prepared, and they are given in Table 1.

The reactions were carried out at  $25 \pm 0.2^\circ\text{C}$  in a thermostatic bath. The final volume water/alkoxide/alcohol was  $200 \text{ cm}^3$  for all compositions. When the dropwise addition was finished, after 2 h, the resulting solutions were poured into closed containers in order to avoid any alteration of the water/alkoxide/alcohol ratio of the mixture. The time required for gelation was inversely related to the zirconium alkoxide con-

centration in the starting mixture. However, a white precipitate of hydrous zirconia oxide particles was obtained for the Zr100 composition.

After gelation, the ‘wet gels’ were dried at  $50 \pm 0.2^\circ\text{C}$  in an oven at room atmosphere for ca. 20 days; thereafter their weight loss was measured and DSC was performed simultaneously. This step is referred as drying process. After this time, the dried gels (xerogels) were heat treated in an electrical furnace at temperatures between 100 and  $1000^\circ\text{C}$ , being this step referred as sintering process.

Drying and sintering processes were studied by DSC measurements carried out in a DSC-7 Perkin–Elmer at a heating rate of  $10 \pm 0.05^\circ\text{C}/\text{min}$  in the temperature range of  $25$ – $500^\circ\text{C}$ . In order to avoid any combustion inside the gel during measurements, a nitrogen atmosphere was used in all experiments. The equipment was calibrated for temperature accuracy, baseline and heat-flow accuracy, using high purity indium and zinc standards.

## 3. Results and discussion

The  $\text{SiO}_2$ – $\text{ZrO}_2$  system is of technological interest due to the possibility of obtaining glasses of high chemical resistance to alkaline solutions [12]. Glass fibres of the  $\text{SiO}_2$ – $\text{ZrO}_2$  system have been used in reinforced concretes [13]. However, in order to obtain glasses of  $\text{SiO}_2$ – $\text{ZrO}_2$  composition it is necessary to use temperatures higher than  $2000^\circ\text{C}$  for melting the corresponding oxides. The sol–gel process opens a new possibility of obtaining such high purity glasses at a very low temperature (ca.  $1000^\circ\text{C}$ ).

As already mentioned, the properties of a xerogel and its calcined product are affected by several parameters and their combinations. If a monolithic xerogel or gel product is desired, a careful thermal treatment schedule must be followed during drying and densification (sintering) processes. The aim of this work was mainly to investigate the drying and densification processes of  $\text{SiO}_2$ – $\text{ZrO}_2$  gels by the DSC technique.

Figs. 1 and 2 show the DSC curves obtained for the different studied xerogels. All these curves show an endothermic peak above  $100^\circ\text{C}$  which is due to the removal of water and alcohols remaining inside the porous gel structure [1,14]. However, the hydrous zirconia precipitate shows the same peak at a

Table 1  
Composition of the investigated solutions

Name	$\text{SiO}_2\%$	$\text{ZrO}_2\%$
Si100	100	—
SZ-84/16	84	16
SZ-50/50	50	50
SZ-25/75	25	75
Zr100	—	100

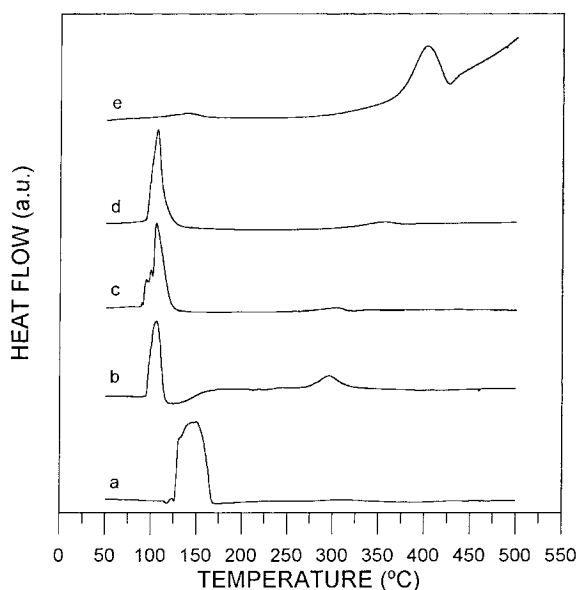


Fig. 1. DSC measured curves for original samples: (a) Si100; (b) SZ-84/16; (c) SZ-50/50; (d) SZ-25/75; (e) Zr100.

temperature close to 140°C. This higher temperature corresponds to a greater difficulty in eliminating water and alcohols from the precipitate structure, in part due to the strong hydrogen bonding between such mole-

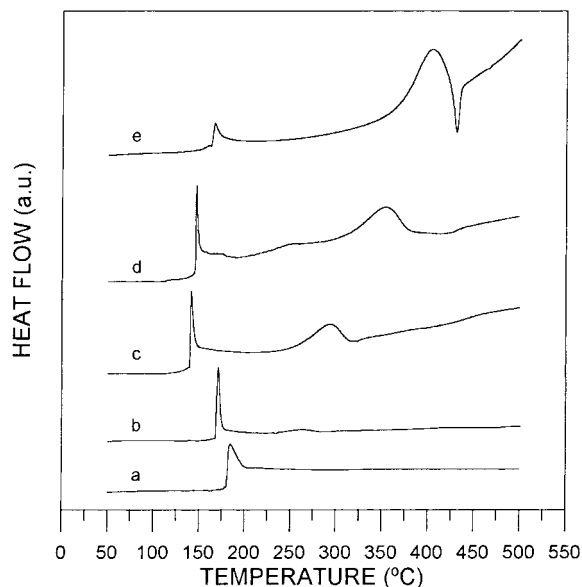


Fig. 2. DSC measured curves for dried samples: (a) Si100; (b) SZ-84/16; (c) SZ-50/50; (d) SZ-25/75; (e) Zr100.

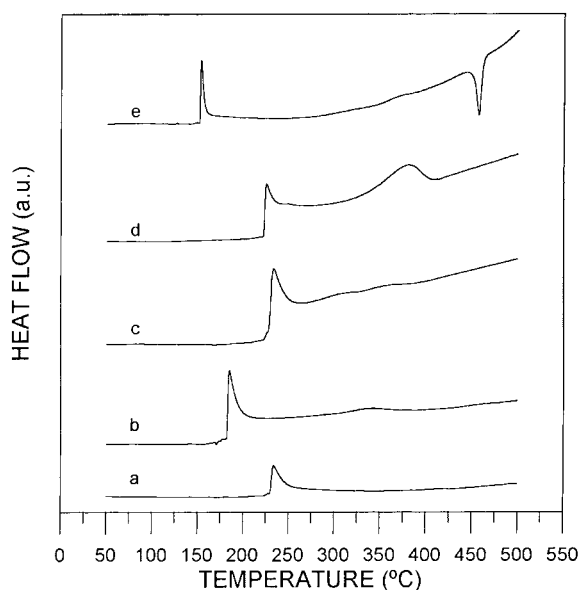


Fig. 3. DSC measured curves for samples heated at 200°C: (a) Si100; (b) SZ-84/16; (c) SZ-50/50; (d) SZ-25/75; (e) Zr100.

cules and the hydrous zirconia oxide particles [15]. Fig. 2 shows the DSC curves of the gels dried at 50°C until no further loss weight was observed (ca. 20 days). Here, an endothermic peak also appears although at higher temperature than 100°C for SiO<sub>2</sub> and SiO<sub>2</sub>-ZrO<sub>2</sub> gels, and above 160°C for the hydrous oxide zirconia precipitate.

Figs. 3–5 show DSC curves of the different studied xerogels heat treated at 200°, 400° and 600°C, respectively. Although, such xerogels have been also treated at 700°, 800°, 900° and 1000°C, no DSC peak has been found for temperatures higher than 800°C, and we may conclude that most part of water and alcohols have been removed at these temperatures.

During the sintering process, the DSC peak corresponding to the evaporation of water and alcohols shifts up to higher temperatures. When samples are heated at 600°C, the presence and observation of any peak is due to two effects, one of them is the presence of closed pores in the gel network [15], and the second is the well-known rehydration process of silica gels [16]. This rehydration process occurs also for the zirconia and silica-zirconia xerogels.

In order to quantify the amount of alcohol and water remaining inside the gel structure after drying or sintering, we have determined the area of the DSC

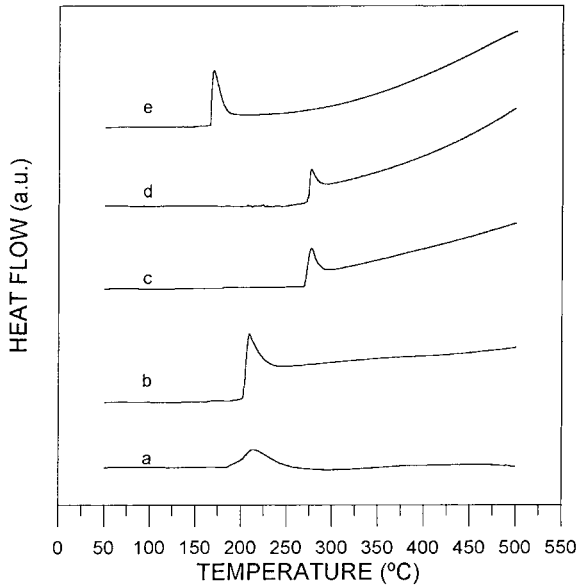


Fig. 4. DSC measured curves for samples heated at 400°C: (a) Si100; (b) SZ-84/16; (c) SZ-50/50; (d) SZ-25/75; (e) Zr100.

peaks being normalized by the sample weight. Figs. 6 and 7 show the evolution of the areas of the DSC peak for the drying and sintering processes, respectively, for the obtained silica, zirconia and silica–zirconia gels.

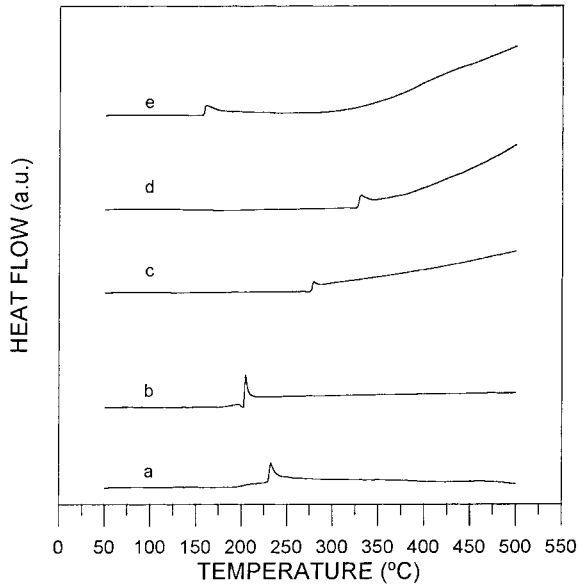


Fig. 5. DSC measured curves for samples heated at 600°C: (a) Si100; (b) SZ-84/16; (c) SZ-50/50; (d) SZ-25/75; (e) Zr100.

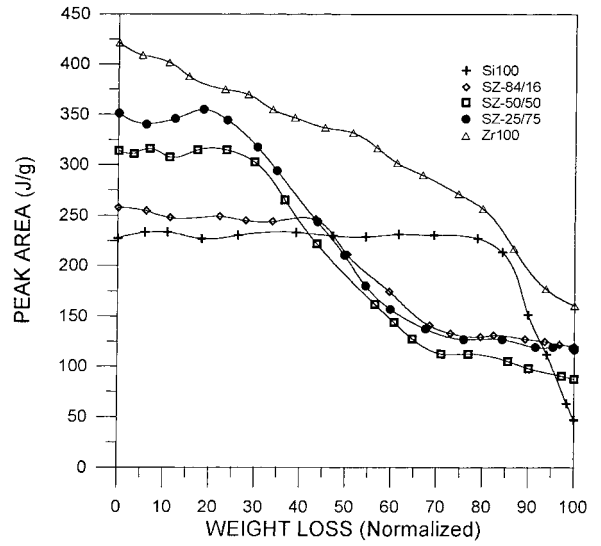


Fig. 6. Variation of the DSC peak area as a function of the normalized weight loss.

In these figures, the weight loss have been normalized to the total weight loss due to the different drying time for each sample. Then, it is possible to make a better interpretation of the results.

Fig. 6 shows different behaviour in the drying process of silica and zirconia gels and an intermediate behaviour is observed for the different silica–zirconia

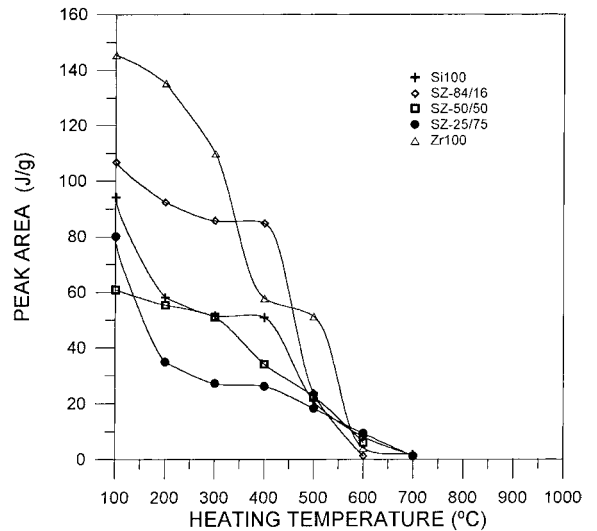


Fig. 7. Variation of the DSC peak area as a function of the heating temperature.

gels. The silica gel shows approximately the same DSC peak area for drying times up to 16 days, and a rapid decrease occurs in the next days. This decrease is due to the elimination of water and alcohols from the pores of the gel causing the well-known gel breakage as it has been showed in different works [17–19]. This behaviour has also been observed for silica gels obtained for different water/alkoxide ratios [1]. On the other hand, the hydrous zirconia oxide precipitate shows a continuously decrease of the area of the DSC peak. This result corresponds to an evaporation of water and alcohol from the very small zirconia particles because a continuous network (monolithic) has not yet been formed.

The mixed silica–zirconia gels show an intermediate behaviour as already mentioned. They show a plateau as the silica xerogel and after a given drying time a continuous decrease is observed as the zirconia precipitate. The drying times related to the plateau are higher as the  $\text{SiO}_2$  concentration in the xerogel is increased. These drying times are 16, 25 and 22 days for the SZ-84/16, SZ-50/50 and SZ-25/75 xerogels, respectively.

It is also observed, in Fig. 6, that the area of the DSC peak of the first drying day is related to the  $\text{ZrO}_2$  concentration, being higher as the  $\text{ZrO}_2$  increases in the wet gel. The high value is therefore observed for the hydrous zirconia oxide precipitate. This result shows that the  $\text{ZrO}_2$  primary particles retain more water and alcohols than  $\text{SiO}_2$  primary particles due to their different pore structure [20,21]. Hydrous zirconia precipitate is formed by small particles of microporous texture (pore radius lower than 10 Å), however silica particles are mainly mesoporous (pore radius between 10 and 200 Å). Water and alcohols are more strongly retained inside micropores than in the mesopores due to the high surface energy of the pore walls. This results in a high retention of water and alcohols in the hydrous zirconia oxide precipitate and also the observed decrease as the  $\text{SiO}_2$  concentration in the xerogel is increased.

Fig. 7 shows the evolution of the area of the DSC peak for the studied xerogels heat treated between 200° and 1000°C. For all the samples, a rapid decrease of the peak area at heating temperatures close to 200°C is observed. After that temperature a slow decrease is observed, and between 500–800°C the peak disappears. For the silica xerogel the DSC peak

disappears between 700–800°C, in accordance with the results of Young [16]. The hydrous zirconia oxide precipitate shows a small DSC peak when it is heat treated at 600°C, and no peak is observed at the treating temperature of 700°C. This temperature, lower than the one of the  $\text{SiO}_2$  xerogel, shows the easier formation of Zr–O–Zr bonds from the Zr–OH groups of the hydrous zirconia precipitate. It is well known that anatase is rapidly formed at ca. 500°C from the amorphous hydrous zirconia precipitate [22]. This crystallization corresponds to the formation of Zr–O–Zr bonds from Zr–OH groups. On the other hand, Si–OH groups do not crystallize and the amorphous structure of the silica xerogel is maintained up to 1000°C.

The binary  $\text{SiO}_2$ – $\text{ZrO}_2$  xerogels shows, in all cases, the disappearance of the DSC peak at heating temperatures lower than those of hydrous zirconia precipitate and the silica xerogel, being lower as the  $\text{ZrO}_2$  concentration in the xerogel is increased. It is observed in Fig. 7 that the disappearance of the DSC peak occurs at 500°, 600° and 700°C for the SZ-84/16, SZ-50/50 and SZ-25/75 xerogels, respectively. This result seems to be associated to the formation of Si–O–Zr bonds from condensation of Si–OH and Zr–OH groups, being such reactions dependent on the Zr–OH concentration in the xerogel. However, it has been shown that when  $\text{SiO}_2$ – $\text{ZrO}_2$  glasses are prepared by the sol–gel process, a network structure similar to glass is formed in the gel, and when the gel is converted to glass on heating to high temperatures, the  $\text{Zr}^{4+}$  ions occupy positions in the interstices of the silica network structure [10]. This result shows that  $\text{Zr}^{4+}$  ions are acting as network modifiers. This result is in accordance with Lee and Condrate [23] and Nogami [10] that showed, by infrared spectroscopy, that the activation energy needed for the dissociation of silica hydroxyls decreases as the  $\text{ZrO}_2$  concentration in the xerogel is increased. Therefore, the temperature at which the DSC peak disappear corresponds to a dehydroxylation of the xerogel by the formation of Si–O–Si bonds where the  $\text{Zr}^{4+}$  ions are incorporated as network modifiers.

As already mentioned, the DSC technique also allows to determine the temperature at which alcohols and water are removed from the gel structure. This temperature corresponds to the interval at which the DSC peak appears and, in a simple way, can be

ascribed to that of the maximum of the DSC peak. If the area of the DSC peak is used to determine the amount of water and alcohols remaining in the gel after drying and sintering, the temperature of the DSC peak can be used for determining that temperature at which alcohols and water are mainly removed if a drying or sintering process is carried out. Since the gel-to-glass transformation in alkoxide-derived gels is dynamic in nature, i.e. the viscosity of the gel increases continuously, and is also dependent on several parameters (gel mass, chemical composition, pH, etc.), different drying and sintering schedules are normally used [1,7]. In this case, the removal of water and alcohols from the gel occurs at different temperatures, even the rest of parameters are maintained constant. This situation can be studied by analysing the temperature of the DSC peak.

In a previous work [1], we showed that the temperature of the maximum of the DSC peak is useful in order to characterize the evolution of silica xerogels. This temperature is related to the availability of hydroxyl condensation between M–OH groups (where M is Si and/or Zr in this work), and also to the evaporation of water and alcohols from closed pores of the xerogel structure. In the present work, the hydrous zirconia oxide precipitate do not form a continuous structure where closed pores are present, however for the other studied compositions monolithic xerogels are obtained and there exists both open and close pores from which desorption is produced.

Figs. 8 and 9 show the variation of the temperature of the DSC peak for the studied gels for the drying and consolidation processes, respectively. In all cases, the temperature of the DSC peak increases with time, being such increase higher in the sintering process. In the drying process, the temperature of the DSC peak mainly increases at the end of drying, and this result corresponds to an easier removal of water and alcohols from a highly open gel structure. It is well known that during the drying process most part of alcohols and water are removed from the gel since the gel structure is not even hardened. A progressive shrinkage and hardening, a stress-development and then fragmentation are the three events normally observed during the drying process of alkoxide-derived gel. In practice, very high drying times are necessary to preserve monolithicity. The results obtained in this work, Figs. 6 and 8, have shown that most part of the water

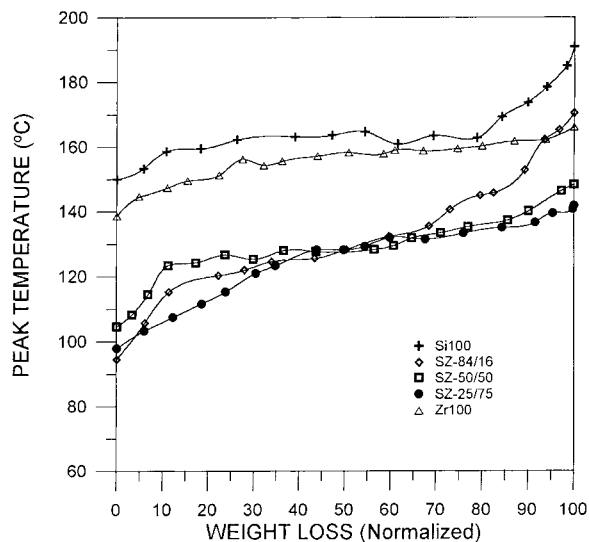


Fig. 8. Variation of the DSC peak temperature as a function of the normalized weight loss.

and alcohols have been removed during drying from the gel structure and this structure is mainly soft to allow such elimination.

On the other hand, during the sintering process the gel structure is hardened and is more difficult to remove water and alcohols, and this can be observed in Fig. 9 by the continuous increase of the DSC peak

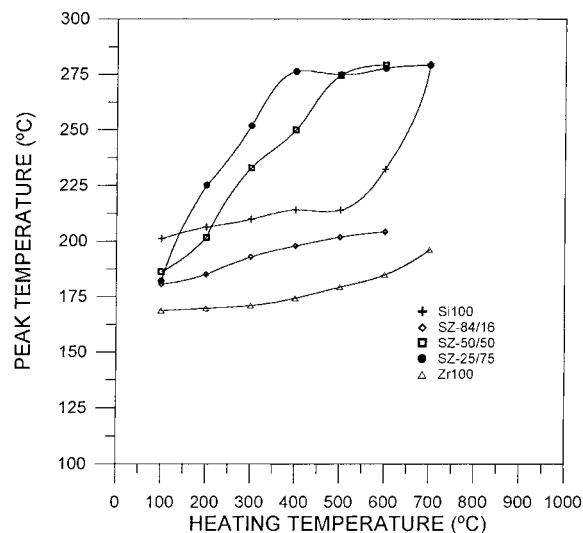


Fig. 9. Variation of the DSC peak temperature as a function of the heating temperature.

temperature. Fig. 9 also shows different behaviours for the studied gels. The  $\text{SiO}_2$  gel shows a continuous increase of the temperature of the peak for sintering temperatures of 100° and 200°C, then is observed a slow increase from 200° to 500°C, and finally a strong increase at the end of the treatment. This result is in accordance with the evolution of the specific surface area and pore volume of alkoxide-derived silica gels. In this case, the surface area and pore volume increases continuously up to 400°C, and then decreases abruptly for higher treating temperatures [7], and this is related to the higher difficulty of removal water and alcohols for the higher treating temperatures.

The hydrous zirconium oxide precipitate shows a slow increase of the DSC peak temperature for treating temperatures between 100° and 200°C, and an abrupt increase at 300°C and finally a continuous increase up to the end of the heat treatment. A similar behaviour has been obtained by Yoldas [24] while studying density values of hydrous zirconium oxide precipitates, and can be assigned to the shrinkage of the powder during consolidation process during which the removal of water and alcohols from the precipitate is difficult. The other silica–zirconia compositions show intermediate behaviour as it corresponds to their compositions. The SZ-84/16 sample presents a similar behaviour than  $\text{SiO}_2$  sample due to the high content in this compound showing a continuous increase up to 500°C and after this temperature no peak was observed. However, the SZ-50/50 and SZ-25/75 show a rapid increase in the peak temperature up to 400°C and after that a stabilization until the disappearance of the peak. It seem that in these two samples the  $\text{SiO}_2$  concentration has an important influence in the peak temperature when they are heated up to 400°C and after this temperature the main influence is due to the  $\text{ZrO}_2$  content.

#### 4. Conclusions

This work has shown the usefulness of the DSC technique for studying the drying and sintering processes of  $\text{SiO}_2$ – $\text{ZrO}_2$  gels. This study has been carried out by a care examination of the area and temperatures of the DSC peaks. The following conclusions can be addressed in this work:

1. During the drying process water and alcohols are removed from the gels. This elimination is continuous for the  $\text{ZrO}_2$  gel, however the  $\text{SiO}_2$  gel shows such removal at the end of the process. The binary  $\text{SiO}_2$ – $\text{ZrO}_2$  gel show an intermediate behaviour depending on their  $\text{SiO}_2$ – $\text{ZrO}_2$  composition.
2. During the sintering process removing of water and alcohols and also hydroxyl condensation occurs. For the  $\text{SiO}_2$  gel, the DSC peak is observed for a sintering temperature up to 700°C, but such peak does not appear at 800°C. This result is in accordance with the dehydroxylation of silica gels. On the other hand the sintering of  $\text{ZrO}_2$  gels shows a DSC peak up to 600°C, result which is associated to the crystallization of  $\text{ZrO}_2$  gels from amorphous to anatase structure.
3. The presence of  $\text{ZrO}_2$  in  $\text{SiO}_2$  gels favours the elimination of water, alcohols and also the hydroxyl condensation. This is observed by a decrease of the temperature of the DSC peak as the  $\text{ZrO}_2$  concentration is increased.
4. The DSC peak temperatures show a little increase during the drying process, and a strong increase is observed during the sintering process. These results show the strengthening of the gel structure during sintering.

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