

## A thermal study of sol–gel silica doped with Fe(II)

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### Abstract

Silica doped with Fe(II) has been prepared using the sol–gel technique. The reactions were hydrolysis and condensation yielding  $\equiv\text{Si}-\text{O}-\text{Fe}-\text{O}-\text{Si}\equiv$ . The compounds obtained were characterized by thermal analysis (TGA and DTA) which indicates the changes that occur in the gel.

### INTRODUCTION

The sol–gel process is a new method which is applied to the preparation of glasses or catalysts [1–4]. This method involves the transformation of a homogeneous solution or sol, formed by an alkoxide, the appropriate alcohol, water and a metallic salt, into a gel. Using this process the molecular structure of the product can be controlled by changing the reaction conditions, as well as the pH, the solvent or the water concentration. An advantage of the technique is that it is relatively easy to introduce iron into the network formed by the alkoxide [5–8].

In the present study, the solids were prepared from tetraethoxysilane and  $\text{FeCl}_2$  under basic pH conditions. In the samples obtained, some of the iron forms bonds with the oxygens of the silica tetrahedron ( $\text{Si}-\text{O}-\text{Fe}-\text{O}-\text{Si}$ ). The rest of the iron is attached to the surface through the terminal silanols ( $\text{Si}-\text{OH}$ ) [9].

### EXPERIMENTAL

#### *Fe-0.1 sample*

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (0.018 g) (Baker, 99% pure) was dissolved in 12 ml of water and 3 ml of  $\text{NH}_4\text{OH}$  (Baker, 99% pure). The solution was refluxed at  $80^\circ\text{C}$  with constant stirring. Tetraethoxysilane (TEOS) (18.6 ml) (Alfa

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Products, 99% pure) was added dropwise. Refluxing was continued until the gel formed. The ion concentration in the final solid was 0.1 wt. %.

#### *Fe-1.0, -2.0, -3.0 and -15.0 samples*

These were prepared as described above, but with differing amounts of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ .

The samples were analyzed in a Shimadzu DT-30 thermal analyzer coupled to an R-123T plotter. Measurements were made in the range 20–800°C in an air atmosphere, at a heating rate of 20°C min<sup>-1</sup>.

#### RESULTS AND DISCUSSION

Figure 1a) shows the thermogram of the Fe/SiO<sub>2</sub>-0.1 sample. The loss of 14% in weight between 20 and 160°C is due to the reaction between the water and ethanol that are occluded into the network when the sol reaches the gelation point. This weight loss is associated with the intense endothermal peak at 100°C, see Fig. 1b). There is a shoulder at 190°C due

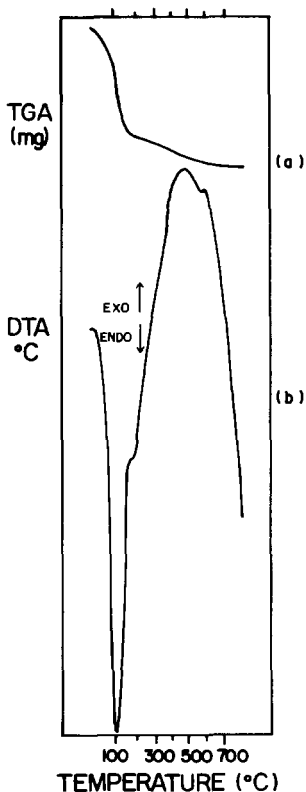


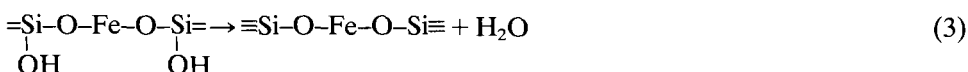
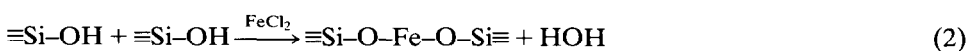
Fig. 1. Thermal analysis of the Fe-0.1 sample from 20°C to 800°C: a) TGA; b) DTA.

to the desorption of unreacted tetraethoxysilane: in this sample it is small. Between 100°C and 800°C there is only a 4% loss in weight, as shown by the endothermic peak at 570°C attributed to the dehydroxylation of the silica [9]. The reactions can be summarized:

Hydrolysis



Condensation



This dehydroxylation occurs at high temperature because hydrogen bridges are present in the silica network so that it is difficult to break the Si–OH bond.

Figure 2 shows the thermogram of Fe/SiO<sub>2</sub>–1.0 which can be interpreted

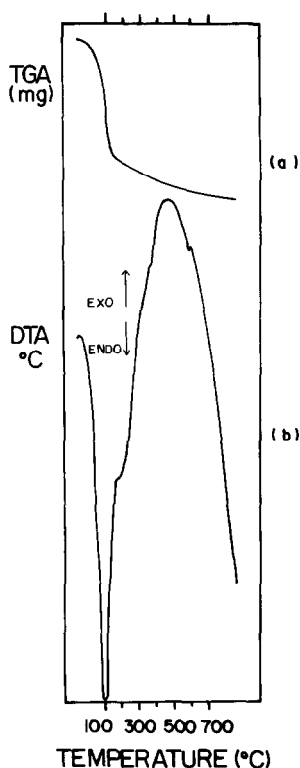


Fig. 2. Thermal analysis of the Fe–1.0 sample from 20°C to 800°C: a) TGA; b) DTA.

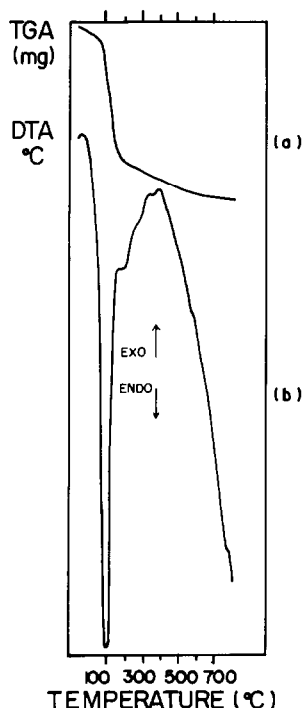


Fig. 3. Thermal analysis of the Fe-2.0 sample from 20°C to 800°C: a) TGA; b) DTA.

as for the first sample. The only difference is that the small endothermic peak is observed at 500°C and continues to 680°C. The concentration of the iron is, indeed, higher.

The samples with 2% and 3% iron (Figs. 3 and 4) show one weight loss, 17% and 15% respectively. The corresponding intense endothermic peaks are found at 100°C (with a shoulder at 200°C) for 2% iron at 95°C (with a shoulder at 190°C) for 3% iron. In both cases an endothermic peak at 375°C is observed which has to be attributed to the loss of hydroxyls. When 3% iron is present, there is another dehydroxylation at 580°C.

When the iron concentration is increased to 15%, the same changes are observed. The first weight loss of 7% occurs from 20 to 98°C. The endothermic peak is less intense than those observed in the other samples; therefore the amount of ethanol and water occluded in this gel was lower. There is a second weight loss between 100 and 230°C (15%) and an intense endothermic peak is found at 225°C. This endothermic peak was not observed in the other gels and can be attributed to the desorption of unreacted ethoxy groups in the alkoxide. The silica formed contains a large amount of organic groups which carbonize at 360°C and 395°C, as shown by the two endothermic peaks [10] (Fig. 5). The solid will then be highly concentrated in surface iron which will be oxidized to form Fe(III). Lastly, a small -OH loss is registered at 590°C.

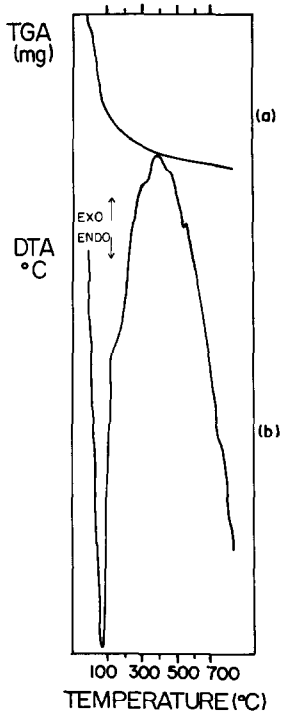


Fig. 4. Thermal analysis of the Fe-3.0 sample from 20°C to 800°C: a) TGA; b) DTA.

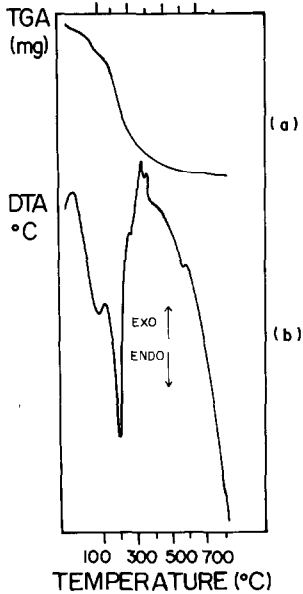


Fig. 5. Thermal analysis of the Fe-15.0 sample from 20°C to 800°C: a) TGA; b) DTA.

Thus, the structural and microstructural changes of the gel take place between 70 and 600°C; above this temperature the solid is stable.

## CONCLUSIONS

Thermal analysis provides an explanation of the changes that occur in the gel, which can be described first as a colloid and then as having the characteristics of a stable solid.

The water and ethanol that were occluded before the gelation point are lost; then the solid is dehydroxylated if the iron concentration is high. The dark appearance of the gels is due to the carbonation of organic residue. The solid is stable at 600°C.

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