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A thermal study of the SiO_2–ZrO_2 sol–gel system

T. López *, M. Asomoza and R. Gomez

Universidad Autonoma Metropolitana Iztapalapa, A.P. 55-534 México D.F. 09340 (Mexico)

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Abstract

Silica–zirconia materials were synthesized by the sol–gel process at pH 3 and 9. The synthesis precursors were tetraethoxysilane and zirconium acetate. The zirconia concentrations were 1.3%, 4.0% and 6.7%. The results obtained show that at pH 3 the tetragonal phase is present; at pH 9, the monoclinic phase is more stable. Thus, when the zirconia concentration is lower, the more stable crystalline phase is obtained in a number of steps.

INTRODUCTION

One of the most important characteristics of zirconia is its ability to improve the stability of other oxides used as catalyst supports. Improvements in stability are usually understood as the stabilization of a high surface area even with thermal treatment. A specific advantage of ZrO_2 over other oxides has been suggested by Colomban and Mazerolles [1]: with zirconia, there is a moderate interaction between the Zr cations and the surface oxide anions, leading to a favourable catalytic effect [2–4].

Nogaro and Kato [5] report the preparation of mixed zirconium aluminium oxides to be used in complex ceramic components. DeLiso et al. [6] propose that, in acid pH, the charge of both oxides is of the same sign and the electrophoretic mobilities of alumina and zirconia are similar in magnitude. Hence, the dispersion is good.

Zirconia is one of the metallic oxides whose properties are simultaneously acid–basic and oxide–reduction. Therefore it is very useful in the catalysis of reactions such as alcohol dehydration or hydrocarbon dealkylation [7]. Zirconium oxide can also exist in different allotropic forms depending on the synthesis method and the calcination process.

The studies on the crystalline properties of zirconia refer, in general, to the monoclinic phase which is the most stable phase at room temperature. Although tetragonal zirconia can be obtained at room temperature by crystallizing an amorphous precipitate at around 500°C, it is very unstable

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* Corresponding author.

and it decomposes to monoclinic zirconia at 800°C. The monoclinic variety is subsequently transformed to tetragonal zirconia at 1200°C; this transformation can be reversed [8, 9].

The preparation method of these materials is very important, because the crystalline phase and the interactions of the Zr^{4+} ion with the oxide with which it is mixed depend on the initial synthesis conditions.

In the present work, zirconium acetate is mixed with a silica alkoxide, tetraethoxysilane. The sol–gel method [10–14] was followed; this method has been used extensively to produce silica particles in the sub-micron range. The solids were characterized by DTA and TGA to determine the temperature at which zirconia crystallizes into the silica network.

To control the processes of crystallization and dehydration of amorphous inorganic hydrogels, we have previously studied the effect of pH on the specific areas and on the acidity of the material [15]. The features of the chemical bond between Zr^{4+} and OH^-, after gelification, are significantly influenced by the dehydration because the dehydration is highly dependent on the metal–hydroxyl interionic dehydration.

EXPERIMENTAL

Two different catalysts were prepared, SiO_2–ZrO_2 in an acid medium (pH 3) and in a basic medium (pH 9). The gelification took place as follows:

A mixture of 36.8 ml of tetraethoxysilane (Aldrich, 99.9%), 10 ml of HCl (Baker, 36% vol.) and 50 ml of ethanol (Baker, 99.9%) was refluxed and stirred. An aqueous solution of zirconium acetate (Baker, 99.9%) was dropped into this solution. The reaction is complete 5 h after the gel is formed. The following zirconium acetate solutions were prepared: 0.293 g of zirconium acetate (1.3 wt.% of ZrO_2); 0.879 g (4.0 wt.% of ZrO_2); and 1.465 g (6.7 wt.% of ZrO_2).

The oxides gelificated in basic medium were prepared in the same way, but instead of adding HCl in the first step of the reaction, NH_4OH (Baker, 33% of NH_3 in water) was added until pH 9 was reached.

The resulting gels were dried at 60°C for 12 h. They were then analysed in a Shimadzu model DT-30 in N_2 atmosphere. The heating rate applied was 10°C min^{-1}.

RESULTS AND DISCUSSION

When zirconium acetate gelificates with tetraethoxysilane by the sol–gel process, an amorphous SiO_2–ZrO_2 mixed oxide is obtained. These results were confirmed by X-ray diffraction. The zirconium oxide crystallizes into the silica network and changes to different crystalline phases by calcination. The results were observed by thermogravimetric analysis and differential thermal analysis.

SiO_2–ZrO_2 (pH 3)

In the thermogram of the silica–zirconia synthesized at pH 3 (1.3 wt.% of ZrO_2), a low intensity endothermic peak is observed at 80°C (Fig. 1), due to the desorption of water and of the ethanol occluded in the gel after the gelification point. At 240°C, a small endothermic shoulder is seen resulting from the desorption of tetraethoxysilane residue.

The first exothermic peak is observed at 280°C; it is characteristic of the crystalline phase changes. At this temperature, the amorphous zirconia forms tetragonal zirconia [16]. At 1090°C, an intense exothermic peak is observed as all the zirconia becomes monoclinic ZrO_2.

The total weight loss of the sample is 10%, due to the desorption of water, ethanol and organic residues in the gel, resulting in partial dehydroxylation of the silica, leaving only silanol groups (≡Si–OH) strongly bonded. The solid network suffers a considerable contraction due to the crystalline rearrangements.

When the concentration of the zirconium oxide in the silica matrix is increased to 4%, the zirconia does not crystallize at 280°C, see Fig. 2. The first exothermic peak is observed at 900°C, indicative of the existence of the monoclinic phase. However, at 1000°C another peak of less intensity is seen, i.e. only a portion of the monoclinic zirconia forms tetragonal zirconia. The endothermic peaks are unchanged in position and intensity: a peak is observed at 85°C and the two shoulders at 220 and 260°C are attributed to the desorption of alkoxide residues and to the partial dehydroxylation of the material. In this solid, the tetragonal phase is

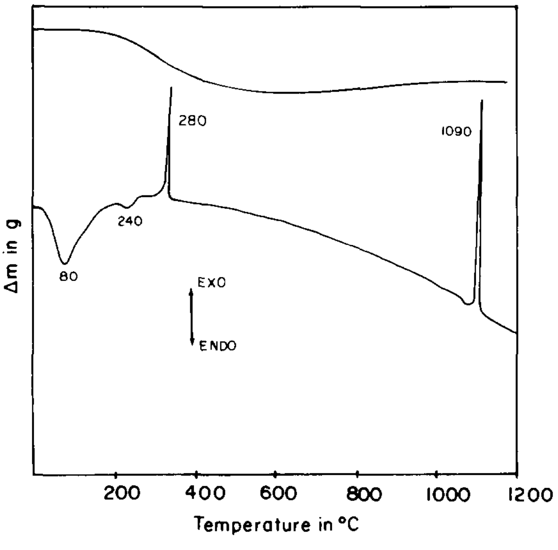


Fig. 1. Thermogram of SiO_2–ZrO_2 (1.3 wt.% ZrO_2) synthesized at pH 3.

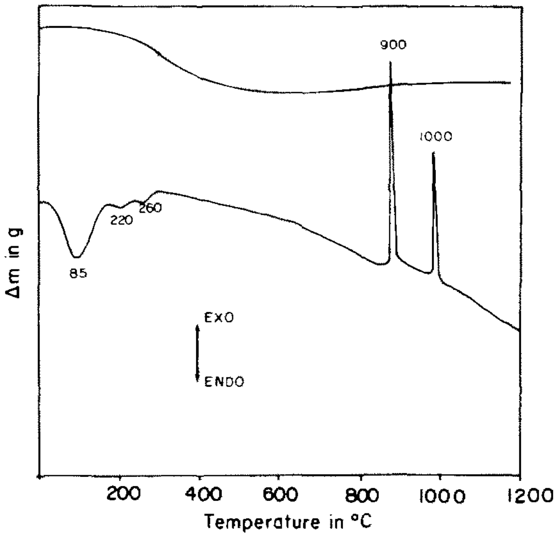


Fig. 2. Thermogram of SiO_2–ZrO_2 (4.0 wt.% ZrO_2) synthesized at pH 3.

formed at a lower temperature than in the material with 1.3 wt.% ZrO_2. The weight loss is also 10%, and the network is again contracted.

If the concentration of zirconia in the sample is 6.7%, the thermogram is very different (Fig. 3). The endothermic peak appears at the same temperature, but the two shoulders are shifted, one to 200°C and the other, caused by the dehydroxylation, to 300°C, because the sample needs more energy for the dehydroxylation. The presence of zirconia inside the silica

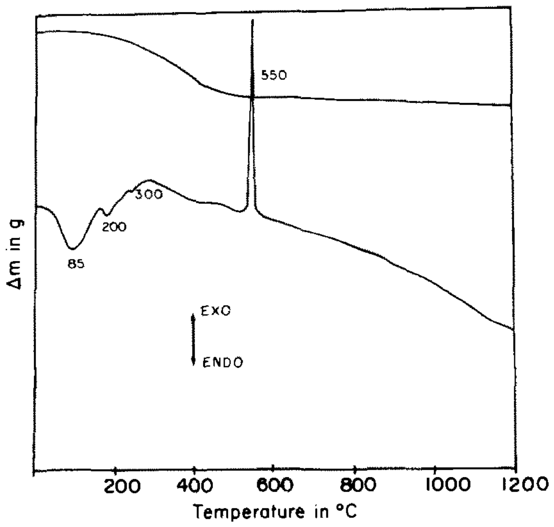


Fig. 3. Thermogram of SiO_2–ZrO_2 (6.7 wt.% ZrO_2) synthesized at pH 3.

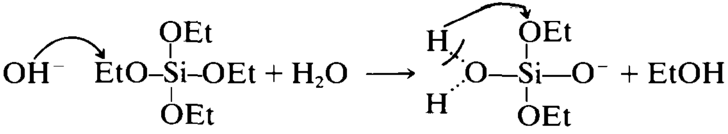
network stabilizes the hydroxyl groups and the OH groups are more strongly bonded to the network of the compound.

Because of a higher concentration of silanol groups ($\equiv$Si–OH), the zirconia changes to the tetragonal phase at 550°C. There is an intense exothermic peak at this temperature, i.e. all the oxide has been transformed to tetragonal zirconia. During calcination to 1200°C, the thermogram is unchanged, and therefore the tetragonal phase is very stable under these reaction conditions. This is important because the tetragonal phase is obtained at temperatures lower than those reported in the literature for solids prepared by other methods.

SiO_2–ZrO_2 (pH 9)

The effect of pH on the gelification is very important because all the physicochemical properties of the material are altered.

At basic pH, a polymerization reaction is favoured and the hydrolysis is not total. The mechanism of the reactions follows a nucleophilic substitution, where the OH^- of the reaction environment reacts with the ethoxy group. Nucleophiles are then formed



$$\mathrm{OH^-}\quad \mathrm{EtO{-}\underset{OEt}{\overset{OEt}{Si}}{-}OEt} + \mathrm{H_2O} \longrightarrow {}^{H}_{H}\mathrm{O{-}\underset{OEt}{\overset{OEt}{Si}}{-}O^-} + \mathrm{EtOH}$$

$$\equiv \mathrm{Si{-}OH} + \equiv \mathrm{Si{-}OH} \xrightarrow{\mathrm{ZrO_2}} [\mathrm{SiO_2}]\mathrm{{-}O{-}ZrO_2} + \mathrm{HOH}$$

In the thermogram of the sample containing 1.3 wt.% of zirconia in silica, there are six exothermic peaks' shifted to lower temperatures when compared to the solids obtained at pH 3 (Fig. 4). Because the crystallization

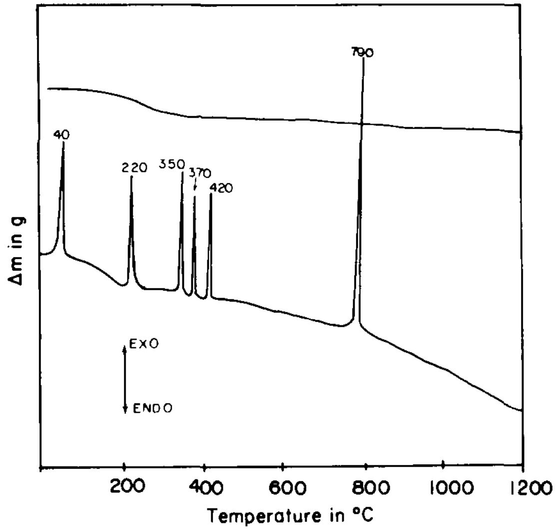


Fig. 4. Thermogram of SiO_2–ZrO_2 (1.3 wt.% ZrO_2) synthesized at pH 9.

temperature is a function of the degree of hydroxylation and the gelification pH, the crystalline phases appear at different temperatures in a basic reaction.

If the gelification pH is 9, the alkoxide hydrolysis is slow and the condensation step is fast; therefore, the resulting structure of the sample has few silanol groups (≡Si–OH), and a large number of ethoxy groups (≡Si–OEt) are retained in the gel [16–19].

In this solid, the first exothermic peak appears at 40°C, indicating that some of the zirconia has been transformed from amorphous to monoclinic. The weight loss is 6% and the network contraction is lower. At 220°C, there is an exothermic peak due to carbonization of the ethoxy groups. Then, three peaks follow at 350, 370 and 420°C, indicating that the tetragonal phase is formed in three steps, and not in one as in the previous cases. The silica sol–gel surface is less hydroxylated. At 790°C, the tetragonal zirconia is transformed to the monoclinic form which is stable even above 1200°C.

It is very important to mention that in these oxides the silica network has a great influence on the crystallization temperature; in the acid gelification oxides, its influence is not so evident.

When the zirconia concentration is 4%, see Fig. 5, a small endothermic peak is observed at 95°C, interpreted as the 5% weight loss of the ethanol and water occluded in the gel. At 880°C, a high intensity exothermic peak indicates that all the zirconia is transformed to the monoclinic form in only one step. Hence, the zirconia concentration has an effect on the crystallization temperature. The lowest concentration causes a crystalline phase transformation in a number of steps.

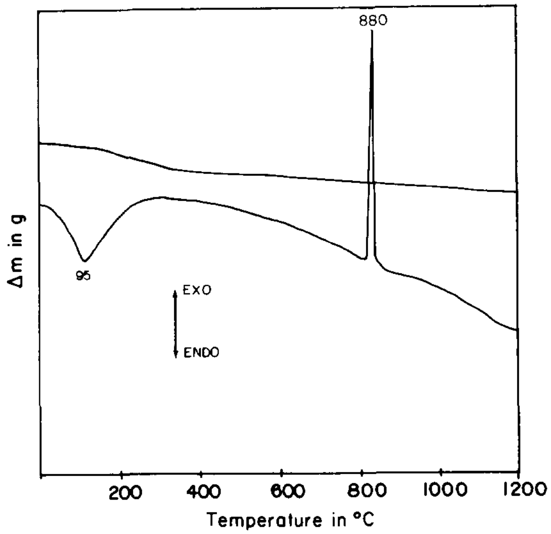


Fig. 5. Thermogram of SiO_2–ZrO_2 (4.0 wt.% ZrO_2) synthesized at pH 9.

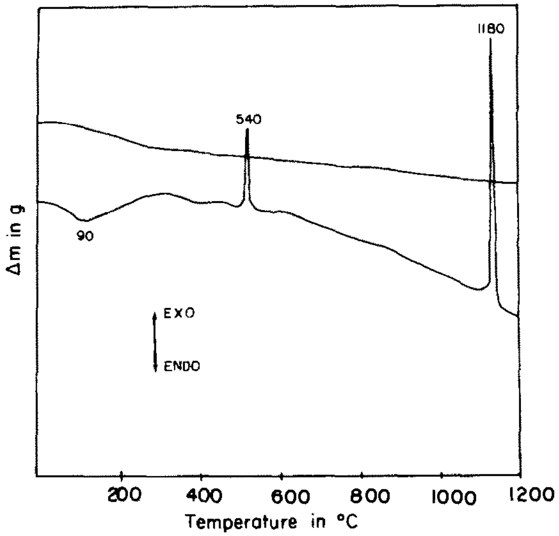


Fig. 6. Thermogram of SiO_2–ZrO_2 (6.7 wt.% ZrO_2) synthesized at pH 9.

When the amount of ZrO_2 is 6.7%, a small endothermic peak appears at 90°C (Fig. 6). At 540°C, the first phase change from amorphous to tetragonal is observed; however, at this temperature only a portion of the oxide is transformed. The rest of the amorphous material transforms to tetragonal phase at 1180°C. In this sample, the monoclinic phase is never observed. The total weight loss is 3.8% and the network contraction owing to calcination is negligible.

CONCLUSIONS

There are three factors that have a direct effect on the crystallization temperature of zirconia: the gelification pH, the zirconia concentration in the silica sol–gel, and the dehydroxylation of the mixed oxides.

When the solids are synthesized at pH 3, the more stable crystalline phase is the tetragonal, but at pH 9 the monoclinic phase is obtained.

The zirconia concentration in the gel is most important. At low contents, the more stable phase is obtained in several steps but if the zirconia content is higher, the main phase is obtained in one step. However, crystallization temperature of zirconia in the silica gel is lower because of a concentration effect.

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