

ZrO₂ obtained by the sol-gel method: influence of synthesis parameters on physical and structural characteristics

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The effects of some synthesis parameters, such as alcohol/alcoxide and water/alcoxide molar ratios, type of solvent and reaction temperature, on the physical and crystalline characteristics of ZrO₂ prepared by the sol-gel method were studied. The results show that gelling time, weight loss, surface area, pore-size distribution and crystalline phases were influenced by the preparation conditions.

1. Introduction

The use of zirconium dioxide as a catalyst or catalyst support in several reactions has been found to be very attractive [1, 2], and is very interesting from a catalytic point of view, because it develops a unique surface chemistry involving both redox and acid-base functions [3]. The need to control the support characteristics has motivated the search for new methods of synthesis. One method to obtain high-purity materials is the sol-gel method, very useful in application in the ceramic industry and in the manufacture of inorganic materials of high technology [4]. Recently, Khan and Ruckenstein [5] have prepared a ZrO₂ catalyst promoted with NaCl via a sol-gel process, which is effective in the oxidative coupling of methane. Taking this into consideration, we have attempted to prepare ZrO₂ via this process. The sol-gel method basically consists in the hydrolysis of an alcoxide to form a sol, followed by gelling, ageing, drying and thermal stabilization. The basic requirement for the alcoxides is that the hydrolysis reaction must be rapid and quantitative. When the alcoxide groups (OR) are stable to hydrolysis, a small amount of mineral or organic acid must be added to effect the reaction. Each step can be controlled and modified in order to obtain a specific material, with high surface area, narrow pore-size distribution, and narrow particle-size distribution.

There are numerous external parameters which affect the reaction rates and the uniformity of the hydrolysis and polymerization [6]. Therefore, the effects of synthesis parameters, such as alcohol/alcoxide and water/alcoxide molar ratios, type of solvent, and reaction temperature on properties such as surface area, pore-size distribution, and crystalline phases, were investigated.

2. Materials and characterization

Methanol, ethanol and butanol were supplied by Merck. The zirconium (IV) propoxide ((CH₃-CH₂

-CH₂O)₄Zr) and a zirconium dioxide used as reference, were from Fluka and the nitric acid was supplied by Panreac.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were carried out in a Perkin-Elmer System 4, under air flow of 200 ml min⁻¹, with a heating rate of 0.5 K min⁻¹. The BET surface areas and the distribution of pore volumes were measured by nitrogen adsorption at 77 K in a Micromeritics ASAP 2000 equipment. The diffraction patterns were measured and evaluated with a diffractometer Philips 1730/10, using CuK_α radiation.

3. Synthesis

The general procedure was as follows. A water solution of HNO₃ was prepared and added dropwise to a reactor containing a solution of the corresponding alcohol and zirconium propoxide under continuous stirring. The time of gelling of the solution was different, depending on the dilution of the samples, the type of solvent and the reaction temperature, as will be discussed later. At the gelling point, the stirring was stopped, and the gel was aged for 5 days at room temperature. The residual alcohol was eliminated by distillation. After the ageing step, the samples were dried in an oven at 353 K for 16 h. The calcination programme involved the samples being heated in air at a rate of 14 K min⁻¹ from room temperature to 573 K, holding at this temperature for 60 min, then heating at the same rate up to 773 K, and maintaining at this temperature for 3 h. The synthesis conditions of the different samples are given in Table I.

The nomenclature used for the samples was as follows. The first number after ZR indicates the content of ZrO₂ (wt%), and the second one, after W (water) gives the H₂O/PrO molar ratio, where PrO = (CH₃-CH₂-CH₂O)₄Zr. H indicates that addition of nitric acid was necessary to form the gel. In all cases,

TABLE I Parameters for ZrO₂ synthesis

Sample	Solvent	T(K)	Molar ratios ^a		
			ROH/PrO	H ₂ O/PrO	H ⁺ /PrO
ZR5W5H	Ethanol	296	49.25	5	0.3
ZR10W5H	Ethanol	296	26.73	5	0.3
ZR15W5H	Ethanol	296	17.82	5	0.3
ZR5W20H	Ethanol	296	49.25	20	0.3
ZR5W40H	Ethanol	296	49.25	40	0.3
ZR5W5H40	Ethanol	313	49.25	5	0.3
ZR5W5H60	Ethanol	333	49.25	5	0.3
ZR5W5HM	Methanol	296	70.81	5	0.3
ZR5W5HP	Propanol	296	37.75	5	0.3
ZR5W5HB	Butanol	296	30.61	5	0.3

^a PrO: (CH₃-CH₂-CH₂O)₄Zr.

ethanol was used as solvent, except in the last three samples, where the last letter indicates the solvent used (methanol, propanol or butanol). In addition, the last number which appears in some samples is the reaction temperature (°C). In the samples where this is not indicated, synthesis was performed at room temperature. Thus, for example, sample ZR5W5H40 was prepared with a concentration of PrO corresponding to the 5% ZrO₂ by weight, an H₂O/PrO molar ratio of 5, with the addition of nitric acid, using ethanol as solvent at a reaction temperature of 313 K (40 °C).

4. Results and discussion

4.1. Effect of the synthesis parameters on gelling time

In order to study the influence of the ROH/PrO ratio on the properties of the formed gel, three oxides with different EtOH/PrO ratios and an H₂O/PrO ratio of 5, were prepared. They are the first three samples in Table I. It was found that the higher the concentration of zirconium, that is, the smaller the EtOH/PrO ratio, the smaller is the gelling time. Therefore, the sample with an EtOH/PrO ratio of 49.25 gels in 30 min; the system with an EtOH/PrO ratio of 26.73 gels immediately after water addition has ceased; and the system with a ratio of 17.82 gels instantaneously, even before water addition has finished. These results agree with those obtained by Montoya *et al.* [7] and Yoldas [8] in the preparation of TiO₂ oxides.

Three samples with H₂O/PrO ratios, of 5, 20 and 40, respectively, and with a constant content of ZrO₂ of 5 wt%, were prepared. When the ratio was 5, gelling occurred in 30 min. Yoldas [8] found that with the same ratio and a TiO₂ content of 5 wt%, gelling occurred in 1 h, and for higher H₂O/alcoxide ratios, the gel was formed almost immediately. This is also what occurred in the present work, because the sample with an H₂O/PrO ratio of 20 gelled in only 5 min. However, a sample with an H₂O/PrO ratio of 40 gelled after 4 h. This must be due to the existence of a critical concentration of water, above which, the gel is not well formed. Probably, the excess of water causes a very fast hydrolysis of the alcoxide, consuming all the disposable OR groups. The near-complete removal of OR groups from the molecular structure causes the

condensation of the particles in these systems, because the presence of a small amount of OR groups is necessary to produce the solubility in alcohol.

The reaction temperature exerts an inverse effect on the time of gel formation. That is, the higher the reaction temperature, the shorter is the gelling time. So, for a reaction temperature of 296 K, the gel is formed in 30 min, whereas if the reaction temperature is 333 K, gel formation occurs in only 3 min (12 min at 313 K).

Four different alcohols were used as solvents in the gelling process. It was found that the higher the number of carbon atoms of the alcohol, the faster was the gel formation. So, in the case of methanol, the gel was not formed in 24 h (studied range), and this sample was not studied further in this work. When ethanol was used, gel formation in the case of sample ZR5W5H occurred in half an hour, as mentioned before. Finally, when propanol or butanol are used as solvents, gel formation is immediate.

4.2. Physical characteristics

The BET surface areas (determined by adsorption of nitrogen at 77 K) of the dried precursors and the calcined samples at 773 K (previously evacuated at 353 and 383 K, respectively), are given in Table II, together with the pore volumes and the average pore radius. The data for the commercial ZrO₂ are also included. The areas of the precursors cover a wide range, from 73–498 m² g⁻¹, although most of them have an area of between 300 and 400 m² g⁻¹.

An effect of the solvent used on the area obtained is observed; the higher the number of carbon atoms of the alcohol, the higher is the area of the precursor obtained. Therefore, the precursor of sample ZR5W5HB, synthesized using butanol as solvent, has an area of 498 m² g⁻¹, compared with 398 m² g⁻¹ of the precursor obtained with propanol (ZR5W5HP) and 282 m² g⁻¹ of sample ZR5W5H, prepared with ethanol as solvent. In addition, the smallest area of this last sample is well correlated with the observation of a more intense shrinking of the gel, which suggests the formation of a denser and less porous gel.

On the other hand, samples prepared with lower molar EtOH/PrO ratios, that is, more concentrated in

TABLE II Physical and structural characteristics of dried and calcined samples

Sample	Dried samples			Calcined samples			
	$S_{\text{BET}}(\text{m}^2 \text{g}^{-1})$	$v_p(\text{cm}^3 \text{g}^{-1})$	$r_p(\text{nm})$	$S_{\text{BET}}(\text{m}^2 \text{g}^{-1})$	$v_p(\text{cm}^3 \text{g}^{-1})$	$r_p(\text{nm})$	$d(\text{nm})^a$
ZR5W5H	282	0.18	1.29	49.6	0.10	4.15	12.6
ZR10W5H	327	0.23	1.44	53.3	0.11	4.20	13.1
ZR15W5H	311	0.24	1.57	49.6	0.11	4.88	13.4
ZR5W20H	344	0.25	1.43	56.1	0.12	4.33	14.3
ZR5W40H	73	0.05	1.36	24.5	0.04	3.65	18.6
ZR5W5H40	323	0.22	1.34	56.2	0.11	4.03	26.9
ZR5W5H60	317	0.20	1.28	48.7	0.10	4.15	13.1
ZR5W5HP	398	0.29	1.45	56.5	0.11	3.98	12.4
ZR5W5HB	498	0.41	1.66	49.9	0.09	3.67	11.3
ZrO ₂	—	—	—	0.6	0.002	4.92	78.1

^a Crystal size determined from the Debye–Scherrer equation.

ZrO₂, show higher areas than the most diluted sample, with an EtOH/PrO ratio of 49.25.

From a study of the effect of H₂O/PrO ratio on the surface areas, it can be seen that for a ratio of 20, an area of 344 m² g⁻¹ is obtained, which is higher than that corresponding to the sample of ratio 5 (282 m² g⁻¹). However, the sample with an H₂O/PrO ratio of 40 suffers a very sharp decrease in area (73.2 m² g⁻¹). This may be due, as explained before, to the existence of a critical concentration of water, above which the gel is not well formed. The decrease in area of this precursor with respect to the others is also correlated to a decrease of pore volume of this sample.

On the other hand, the synthesis temperature does not exert a clear effect on the surface areas.

In calcined samples, the pore structure collapses and the surface area decreases drastically by a factor of 1/6 to 1/10. All the samples have area values of around 50 m² g⁻¹ (in contrast to 0.6 m² g⁻¹ of the commercial ZrO₂), and there are no significant differences between them, with the exception of sample ZR5W40H, previously noted, with an area of around one-half that in the simply dried sample. This last sample, unlike the others, presents a bimodal pore-size distribution, with two maxima, around 1.8 and 3.0 nm, as can be seen in Fig. 1, in which the ordinate scale is arbitrary. Thus, in order to determine the pore volume in the position of the maximum, they are given in it. In the rest of the samples obtained by the sol–gel process, there is only one maximum in the distribution, with the main pore size around 2.5 nm. Unlike them, the ZrO₂ supplied by Fluka has a bimodal distribution, with two maxima, around 2.0 and 6.0 nm. All the samples are fundamentally mesoporous, although ZrO₂ from Fluka has broad mesopores.

4.3. Thermal behaviour

For comparative purposes, and in order to clarify the weight changes observed in the thermograms of the precursors of ZrO₂, thermogravimetric analysis (TGA) of the zirconium propoxide was also carried out. This is depicted in Fig. 2, together with its corresponding differential thermal analysis (DTA). In the TG curve, a first zone of fast weight loss until around 338 K is observed, which can be assigned to the

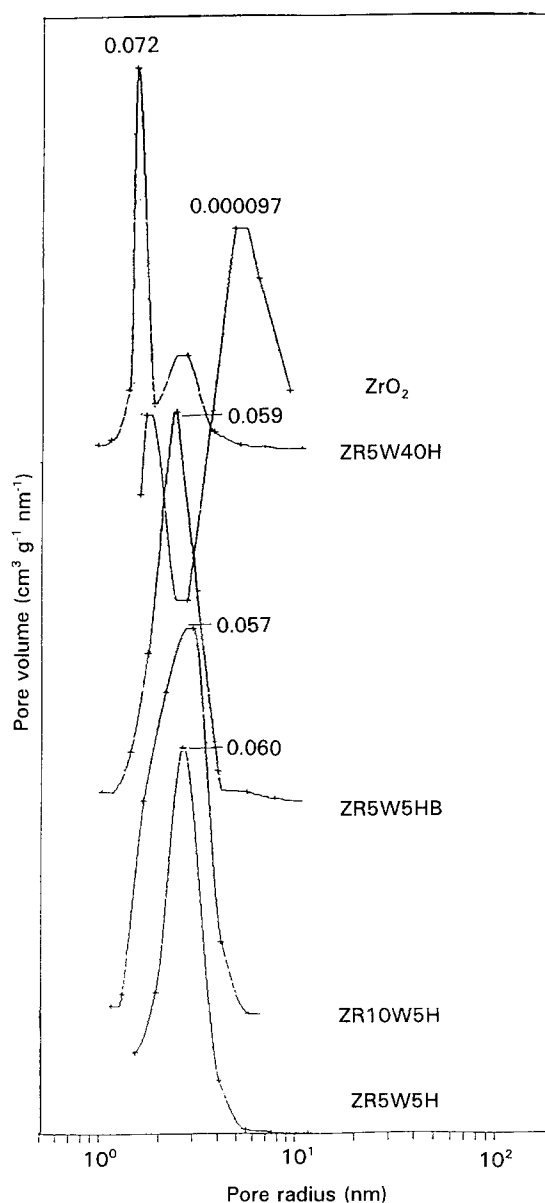


Figure 1 Pore-size distribution of some ZrO₂ calcined samples (nomenclature as in Table I).

removal of the propanol present as solvent ((PrO)₄Zr with 30 wt% propanol). On the other hand, the posterior weight losses observed can be assigned to the removal of the four propoxide groups, leading to the formation of ZrO₂, which remains as a residue.

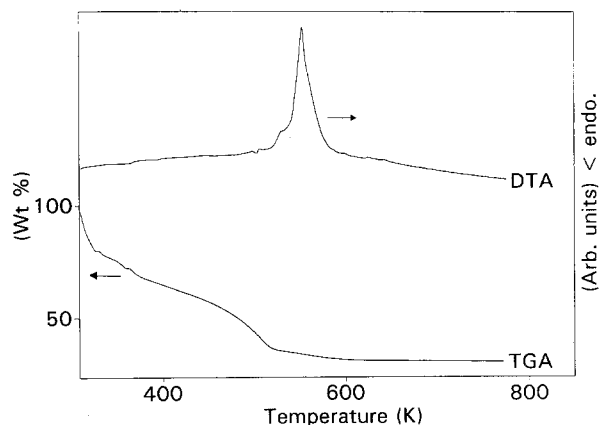


Figure 2 Thermogravimetric and differential thermal analysis curves of zirconium propoxide.

Mazdiyasi *et al.* [9] found that, when zirconium tetratertiary butoxide is pyrolysed, the reaction mechanism from an alcoxide to oxide consists of four steps. In the first one, which is the slow and rate-determining step, the hydrolysis of an OR group is produced. The subsequent hydrolysis of the remaining three alcoxide groups is produced in three successive steps, which are fast. Taking this into account, in the present work, a difference should exist in the thermogravimetric curve of zirconium propoxide between the weight losses corresponding to the first alcoxide group which is removed and those corresponding to the other three groups, which would be equivalent. These two steps could correspond to the zones 338–488 K and 488–613 K, respectively, although the temperature of separation between both steps is not well differentiated. On the other hand, the resulting final residue has a value of 30.51 wt %, that is slightly higher than that corresponding to the complete transformation of the zirconium propoxide in ZrO_2 (26.3 %). This may be the result of the formation of a carbonaceous residue due to the incomplete removal of the total carbon content of the alcoxide group [10]. This is also corroborated by the aspect of the sample after thermogravimetric analysis.

The corresponding DTA of zirconium propoxide is also included in Fig. 2. An exothermic peak is observed in the temperature range 513–613 K, although two other superposed peaks seem to exist in the zone 513–563 K. The total heat evolved in this range of temperatures has a value of 517 cal g^{-1} , which could be associated with a phase transformation, because it corresponds to a near constant weight in the thermogravimetric analysis. In order to study the phases existing before and after the exothermic process, the analysis by XRD of the zirconium propoxide calcined at 493 or 773 K, was carried out. It was observed that, at 493 K, the phase formed was amorphous, and at 773 K, the monoclinic phase of ZrO_2 was obtained. So, it is in this range of temperatures where the transformation of an amorphous to crystalline phase is produced.

The thermogravimetric analysis of some of the samples dried to 353 K are shown in Fig. 3. They were carried out under an air flow of 200 ml min^{-1} , at a

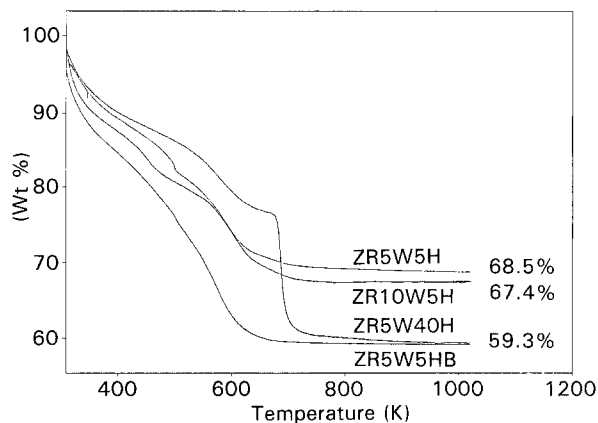


Figure 3 Thermogravimetric analysis curves of some dried samples (nomenclature as in Table I).

heating rate of 0.5 K min^{-1} , because higher rates caused a phenomenon of “explosion” of the sample, of fast decomposition around 463–493 K, with a very sudden weight loss.

Unlike the zirconium propoxide, in the case of the precursors obtained by the sol–gel method, it is difficult to assign a determined weight loss to the removal of a molecule or of a given component. The complexity of the polymeric system of zirconium that can be formed by the hydrolysis, in the presence of bridge and terminal OH groups, and water molecules in variable proportion [11], together with the different conditions used in the formation of the precursors, such as type of alcohol used as solvent and different amounts of alcohol and water, make the assignation difficult of a step of the curve to the removal of a determined component. However, the initial zone of the curve, up to around 473 K could be assigned to the elimination of physically adsorbed water and alcohol, and the rest to the burning of residual organic material and chemically adsorbed water. Only in the case of sample ZR5W40H was a very fast and defined weight loss observed in the range 273–293 K, which could correspond to the removal of two water molecules and the transformation of $Zr(OH)_4$ to ZrO_2 . However, it is known that the hydrolysis of the zirconium alcoxides leads to the formation of oxo and aqua groups rather than true hydroxides [12]. Curiously, this sample has an area four to five times lower than the rest, as noted before.

On the other hand, the final weights of the samples are different, depending on the distinct initial composition of the precursor. In all cases, a constant amount of zirconium propoxide was used, in order to obtain 2.5 g ZrO_2 . However, the amounts of alcohol and water were varied, as also was the type of alcohol used as solvent. Therefore, a weight loss was observed that was larger, the higher was the number of atoms of carbon of the alcohol used. In this way, the final weight percentage observed for sample ZR5W5H, prepared with ethanol, was found to be 68.5%, compared with 66.7% of the sample prepared with propanol (ZR5W5HP, not shown in the figure) and with 59.3% of the sample obtained with butanol (ZR5W5HB).

A higher weight loss was also observed as the H_2O/PrO ratio increased. Thus, sample ZR5W40H,

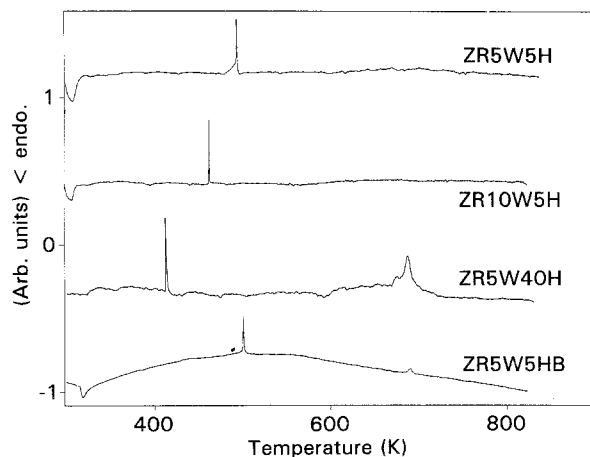


Figure 4 Differential thermal analysis curves of some dried samples (nomenclature as in Table I).

prepared with a ratio $H_2O/PrO = 40$, shows a weight loss 9% higher than sample ZR5W5H, obtained with an H_2O/PrO ratio of 5 and the same ROH/PrO (equal to 5).

In Fig. 4 the corresponding differential thermal analyses are shown. The ordinate scale is arbitrary. In some samples an endothermic peak can be detected up to around 333 K, which can be assigned to the loss of physically adsorbed water. In all the samples a very sharp exothermic peak is observed, which appears in the temperature range 463–503 K, with the exception of sample ZR5W40H, where it is displaced to a lower temperature (413 K). This peak can be assigned to the rapid process of decomposition of the polymeric material formed, or to a possible burning of the organic material, although it does not correspond to a defined weight loss in the thermogravimetric curves. On the other hand, samples ZR5W40H and ZR5W5HB show a second exothermic peak, in the zone of temperatures around 688 K, which corresponds to a near constant weight, and for this reason it could be assigned to a phase transition or to the formation of the crystalline phase. However, although the order of magnitude of the heat evolved in the process is not very significant (only 5 cal g^{-1}), we cannot know why this peak is observed in some cases and not in all of them.

4.4. Crystalline phases

X-ray diffractograms of some of the calcined samples are shown in Fig. 5. For comparison, a diffractogram of a commercial zirconium dioxide (Fluka), is also included. This oxide crystallizes in the monoclinic system. In the rest of the samples, obtained via the sol-gel process, the cubic phase is principally obtained, in agreement with other researchers [13, 14]. This initial cubic phase starts to convert to the monoclinic phase upon heating, which is why trace amounts of the monoclinic phase are observed in the diffractograms, especially in sample ZR10W5H, with a higher ZrO_2 content, where both phases coexist. Yoldas [15] also observed a greater stability of the monoclinic phase when the ZrO_2 was formed under more

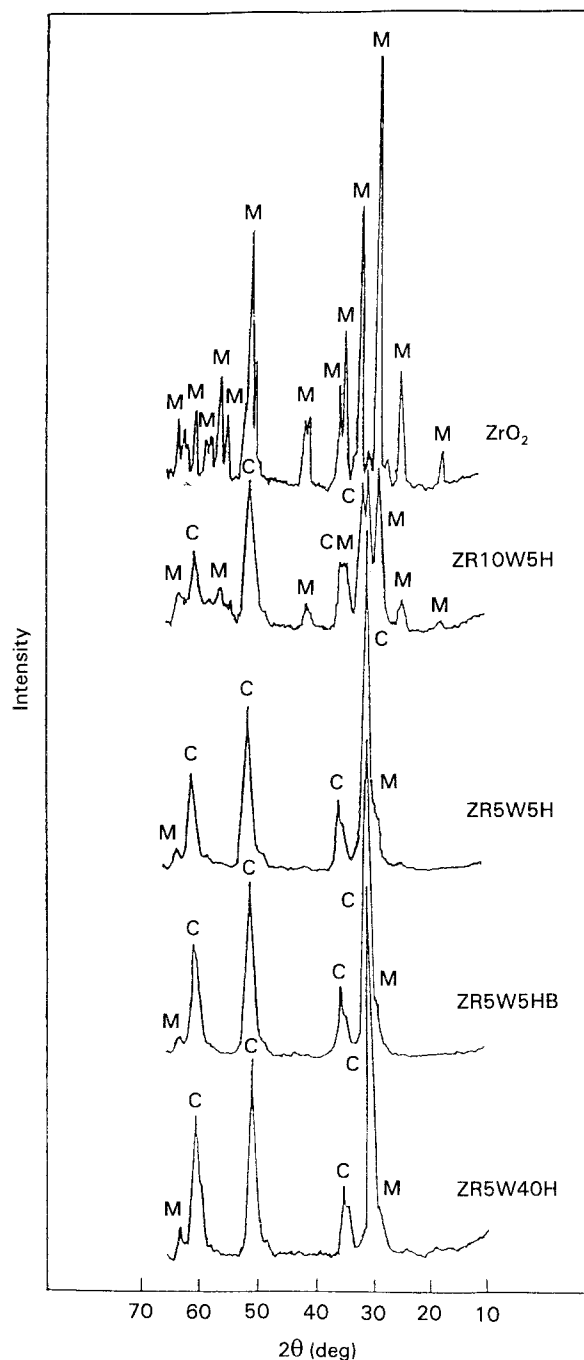


Figure 5 X-ray diffraction patterns of some ZrO_2 calcined samples (nomenclature as in Table I). M, monoclinic phase; C, cubic phase.

concentrated conditions. That sample could be especially interesting because it is generally recognized that the most useful mechanical and refractory properties of zirconia to be used as structural ceramics are obtained in multiphase material known as partially stabilized zirconia (PSZ). Garvie and Nicholson [16] have demonstrated that a fine-scale precipitate of monoclinic zirconia in a cubic stabilized matrix enhances the strength of PSZ.

The crystal sizes of the calcined samples were determined by the Debye-Scherrer equation (from the diffraction peak (1 1 1) of the cubic phase) and they are shown in Table II, together with the crystal size of the commercial ZrO_2 from Fluka. The synthesized samples exhibited crystal sizes between 11.2 and 18.5 nm, except for the sample prepared at the highest temper-

ature, which has a value of 26.91 nm. An increase in the crystal size is also observed when increasing the H₂O/PrO ratio, but it decreases when the number of carbon atoms of the alcohol used as solvent and the ROH/PrO ratio increase. In the case of ZrO₂ from Fluka, the crystal size was determined from the diffraction peak (1 1 $\bar{1}$) of the monoclinic phase, giving a value of 78.1 nm, which is around six times greater than that of the samples prepared in this work.

5. Conclusion

ZrO₂ has been synthesized by the sol-gel method. Variations in the synthesis conditions produce solids of different characteristics. The reaction temperature, the type of solvent and the EtOH/PrO ratio exert a clear effect on the gelling time, so that the higher the temperature and the number of carbon atoms of the alcohol and the smaller the EtOH/PrO ratio, the smaller is the gelling time. However, the effect of H₂O/PrO ratio is not so clear. From the results obtained by thermogravimetric analysis, and due to the complexity of the system and the number of components, it is difficult to assign a determined weight loss to the removal of a given component or molecule, although the final weight depends on the initial composition. Most of the solids obtained have a high value of surface area (between 300 and 400 m² g⁻¹), which decreases strongly down to 1/6 upon calcination at 773 K. The cubic phase was obtained after calcination in most of the samples, although some trace amounts of monoclinic phase were present.

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