Effects of H_2O_2 and SO_4^{2-} Species on the Crystalline Structure and Surface Properties of ZrO_2 Processed by Alkaline Precipitation

J. A. Navio,* G. Colón, P. J. Sánchez-Soto, and M. Macias

Instituto de Ciencia de Materiales de Sevilla, Centro de Investigaciones Científicas, "Isla de la Cartuja", Avda. Américo Vespucio, s/n, Isla de la Cartuja, 41092-Sevilla, Spain

Received December 6, 1996. Revised Manuscript Received February 28, 1997[⊗]

The preparation of ZrO_2 by alkaline hydrolysis of $ZrOCl_2·8H_2O$, leads to an amorphous oxohydroxide precursor that upon calcination at temperatures higher than 350 °C produces a system with mixed crystallographic phases (monoclinic and tetragonal). Preparation of this material by the same procedure but adding different molar ratios of H_2O_2 produces amorphous precursors (ZHP*n*) developing, mainly, the tetragonal crystal phase at the same calcination temperatures. The molar fraction of the phases seems to be dependent on the H_2O_2 molar ratio, thus indicating a direct relationship of this parameter with the crystallization behavior. At a surface level, preparation with H_2O_2 seems to retain NH_4^+ from the alkaline medium even after calcination at 500 °C for 2 h. The sulfation process of these ZHP*n* samples also modifies the structural properties; in this case, the crystallization process is delayed at higher temperatures, but with the same crystallographic features of the nonsulfated series, the tetragonal phase becoming stable for temperatures up to 800 °C.

Introduction

The aqueous chemistry of zirconium is dominated by its tendency to form inorganic polymers based on bridged-hydroxyl groups. The characteristic behavior of these groups allows the production of a great variety of zirconium salts and complexes that could act as catalytic precursors. The nature and size control of these polymers, carried out after and during the precipitation of the precursor, lead to interesting variations in the final properties of the formed oxide.[1] In this sense, the "modeling" of its structural features could constitute a great advance in the design of new catalysts.[1−3] Within the range of the different catalyst preparation methods, precipitation ones are those most used for the preparation of mono- and multicomponent oxide materials. In this group, the sol−gel method allows a good control of the texture, composition, homogeneity, and structural properties of the final product.[4] The 3-D framework generated by particle aggregation of the sol can be extended in a quasi-infinite way, finally forming the gel. The homogeneity of gel depends on several factors such as the solubility of products, the nature of the solvent, the sequence of the hydrolyzing agent, the temperature, and pH.[5]

The first step in the sol−gel processing method is the hydrolysis of the precursor. This step implies reactions between the precursor salt ions and the water molecules forming a solvated ion, surrounded by a hydration sphere whose properties depend on the nature of the ion:

$$M^{z+} + nH_2O \rightleftharpoons [M(H_2O)_n]^{z+}$$

The polarizing effect of the ion over solvated H_2O molecules could produce a dissociation of part of these molecules:

$$[M(H_2O)_n]^{z+} \rightleftharpoons [M(H_2O)_{n-x}(OH)_x]^{(z-x)+} + xH^+$$

Thus the presence of certain additives in this "precursor" solution could affect the nature of the species which will form the gel by condensation (formation of OH bridge and oxo bridge bonds). Previous results using H_2O_2 as reagent in the preparation procedure[6,7] showed the advantages of using this additive in the processing of a zirconium titanate. In that case, the mixed oxide $(Zr,Ti)O_2$, processed in the presence of H_2O_2 showed a lower DTA crystallization peak and textural properties different from those exhibited by the same material prepared in the absence of H_2O_2. That was interpreted by assuming the higher lability of the peroxidic bonds in the 3-D fresh gel that lead to a different behavior during further calcination and crystallization processes.

In the case of a zirconium-based precursor, the influence of the preparation conditions as well as the calcination procedure on the latest catalytic properties of this material could be interpreted as a result of the possible modifications in the structural unit of the precursor hydroxides (Figure 1) proposed by Murase et

---

* Corresponding author.

[⊗] Abstract published in *Advance ACS Abstracts,* April 15, 1997.

(1) Davis, B. H. *J. Am.Ceram. Soc.* **1984**, C-168.

(2) Rouxel, J.; Livage, J. *Rev. Chem. Miner.* **1984**, *21*, 283.

(3) Rouxel, J.; Livage, J. *J. Solid State Chem.* **1986**, *64*, 242.

(4) Cauqui, M. A.; Rodriguez-Izquierdo, J. M. *J. Non-Cryst. Solids* **1992**, *147/148*, 724.

(5) Brinker, C. J.; Smith, D. M.; Deshpande, R.; Davis, P. M.; Hietala, S.; Frye, G. C.; Ashley, C. S.; Assink, R. A. *Catal. Today* **1992**, *14*, 155.

(6) Navio, J. A.; Macias, M.; Sánchez-Soto, P. J. *J. Mater. Sci. Lett.* **1992**, *11*, 1570.

(7) Navio, J. A.; Marchena, F. J.; Macias, M.; Pánchez-Soto, J.; Pichat, P. *J. Mater. Sci.* **1992**, *27*, 2463.

S0897-4756(96)00625-4 CCC: $14.00

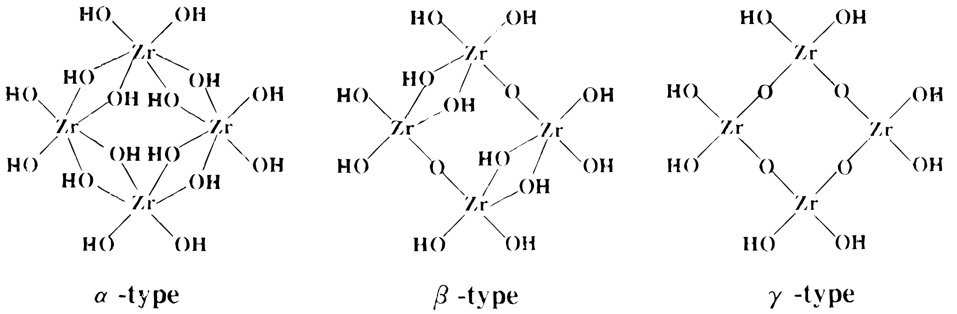


Figure 1. Model structures for hydrated Zr^{4+} polycations.

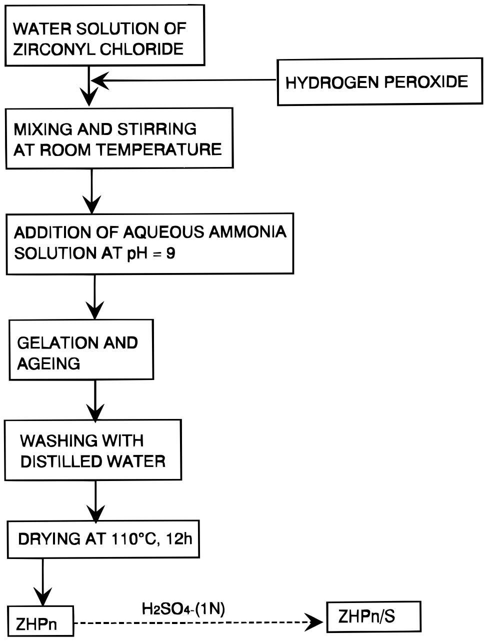
al.[8] by taking the original model of Zaitsev et al.[9] It should be noted that in the α-type hydroxide, the zirconium cations are linked by OH groups, whereas in the γ-type oxo bridges exist between zirconium cations; the β-type represents an intermediate situation between both extreme idealized structures. In this latter case, both OH groups and oxo bridges exist between zirconium cations. Thus α-type hydroxide would be the predominant form when the precursor is obtained by alkaline precipitation. However, an aging process could lead to modifications in the structure of the precursor to reach β-type hydroxide and finally the γ-type one by losing of the bridged OH groups.[9] Upon these considerations the α-type hydroxide is considered as the precursor of the tetragonal ZrO_2, having been reported that the metastable tetragonal phase is becoming of great interest in catalysis,[10−13] especially when used as sulfate-doped ZrO_2.[14]

Due to its potential use in catalysis, ZrO_2 and sulfate-doped ZrO_2 is attracting considerable interest, as catalyst itself and as support for metals and other oxide catalysts.[15−19] Thus, the effect of H_2O_2 addition during the preparation of those materials on the structures and surface properties is interesting and could provide new information.

In the present work we have studied the effects of the presence at the hydrolysis step of the preparation procedure on the crystal phase and spectral features of the ZrO_2. We have tried to modify the structure of the precursor oxohydroxide just in the hydrolysis reaction by adding this peroxidic agent. Finally, the zirconia-precipitated samples were sulfated, and the structural characterization was carried out.

Experimental Section

Scheme 1. Flow Sheet of the Preparation of the Samples (See Text for More Details)



Materials and Methods. Zirconia samples were prepared by slow alkaline precipitation, using an inorganic salt, $ZrOCl_2\cdot 8H_2O$ (Fluka Kemike; AG, 43−44% ZrO_2), as a precursor. The processing route of the samples is shown in detail in Scheme 1. Certain amounts of H_2O_2 (Merck, 30−32 wt % solution in water) were added to the aqueous zirconyl solution, giving molar ratios ZrO_2:H_2O_2 of 1:1, 1:2, and 1:4. The precipitation of the gels was achieved by a slow addition of an aqueous ammonia solution (Merck, 28 wt %) until the pH reached a value of ca. 9. Higher pH values could lead to more hydrated and hydroxylated precursors by the elimination of peroxidic bonds as has been reported by us.[7] Once the pH value is reached, gels were allowed to age for 30 min, after which they were filtered and washed repeatedly with bidistilled water until no Cl^- signal was detected in filtering water ($AgNO_3$ test). Finally, the precipitated gels were dried in an oven at 110 °C for 12 h. Samples thus prepared were called ZHP*n*, "*n*" being the H_2O_2 molar ratios. A further sulfation process was carried out by impregnation of the dried powdered samples with 1 N H_2SO_4 (Merk), by the addition of 3 mL of acid solution/g of powder, with continuous stirring at room temperature. Then, the stirred suspensions were filtered (without washing), and the sulfated samples dried in an oven at 110 °C for 12 h. This set of specimens will be called hereafter ZHP*n*/S. The calcination treatment was performed in an oven by direct exposure to air, at selected calcination temperatures for 4 h.

Techniques. Specific BET surface area measurements were carried out in a Micromeritics 2000 rapid surface analyzer, using N_2 as adsorbate gas.

X-ray diffraction patterns (XRD) were obtained using a Phillips PW1060 diffractometer with Ni filter and graphite monochromator. The X-ray source was Cu Kα radiation.

Infrared (IR) spectra were recorded in a Perkin-Elmer 883 spectrometer; spectra ranged from 4000 to 400 cm^{-1} in the

---

(8) Murase, Y.; Kato, E. *Yogyo Kyokaishi* **1978**, *86*, 226.
(9) Zaitsev, L. M. *Zh. Neorg. Khim.* **1966**, *11*, 1684.
(10) Moles, P. J., Ed.; *Catal. Today* **1994**, *20*, 185.
(11) Silver, R. G.; Hou, C. J.; Eckerdt, J. G. *J. Catal.* **1989**, *118*, 400.
(12) Osendi, M. I.; Moya, J. S.; Serna, C. J.; Soria, J. *J. Am. Chem. Soc.* **1985**, *68*, 135.
(13) Morterra, C.; Cerrato, G.; Feroni, L.; Negro, A.; Montanaro, L. *Appl. Surf. Sci.* **1993**, *65/66*, 257.
(14) Morterra, C.; Cerrato, G.; Pinna, F.; Signoretto, M. *J. Catal.* **1995**, *157*, 109.
(15) Yamagushi, T.; Nakano, Y.; Iizuka, T.; Tanabe, K. *Chem. Lett.* **1976**, 1053.
(16) Yamagushi, T.; Hightower, J. W. *J. Am. Chem. Soc.* **1977**, *99*, 4201.
(17) Nakano, Y.; Yamagushi, T.; Tanabe, K. *J. Catal.* **1983**, *80*, 307.
(18) Imizu, Y.; Sato, K.; Hattori, H. *J. Catal.* **1982**, *76*, 65.
(19) Matsuhashi, H.; Hattori, H. *J. Catal.* **1984**, *85*, 457.

Table 1. Specific Surface Areas for Sol−Gel Processed ZrO_2

sample	nonsulfated	sulfated
ZrO_2	290.0	222.3
ZHP1	157.7	117.7
ZHP2	77.1	60.0
ZHP4	98.1	95.5

transmittance mode of operation. All the samples were mixed with KBr and then pelleted without further treatments.

Results and Discussion

Table 1 shows the specific BET surface areas for the different gels, nonsulfated ZHP*n* and sulfated ZHP*n*/S, dried at 110 °C for 12 h. Also included, for comparison, are the specific surface areas of ZrO_2 prepared by the same precipitation route but in the absence of H_2O_2.

It can be observed that the preparation of zirconia specimens in the presence of H_2O_2 (ZHP*n*) leads to a disminution in the specific surface areas, compared with those shown by zirconia prepared in the absence of H_2O_2 (ZrO_2). A further sulfation process also produces a disminution in the initial S_{BET} values in all cases. The decrease caused by the sulfation process seems to be smaller for the ZHP4 sample, for which sulfation only decreases the initial value of the nonsulfated sample by about 3%. The decrease observed by the sulfation process could be interpreted in the same way as previously reported;[20] the effect of sulfate produces a displacement of the hydroxyl groups, which combined with the thermal treatment, could lead to the collapse of the surface. If we assume that the amount of oxo-bridged bonds is mainly related to the amount of initial peroxidic bonds in the precursor, and taking into account the fact that sulfate species are adsorbed over free hydroxyl groups,[20] then the greater decreases in the S_{BET}, after sulfation, may be expected for samples starting from a more hydroxylated precursor, as is observed for the ZrO_2. The collapse in the S_{BET} could be of minor relevance for the sample ZHP*n*, with an already collapsed surface due to a drastic elimination of peroxidic bonds upon drying.

Figure 2 shows XRD patterns for the processed ZrO_2 calcined at different temperatures for 4 h. The crystallization process takes place at a temperature around 350 °C. As can be observed, over the short temperature range (ca. 350−400 °C), the predominant phase is the tetragonal (T) one with a slight participation of the monoclinic (M) one. This latter phase seems to develop with calcination temperature, becoming predominant for a calcination temperature higher than 550 °C. This fact can be observed in detail in Figure 3, in which the monoclinic molar fraction, X_M, has been plotted vs the calcination temperature. The X_M values have been calculated using the expression and method previously reported by Mercera et al.[21] The X_M value leads to a rapid increase for a temperature higher than 450 °C; thus, the tetragonal phase is predominant only over a short range of temperatures (between 300 and 450 °C).

Regarding ZHP*n* samples (Figure 4), it is worth noting that the XRD patterns for these samples calcined at 400 °C 4 h showed well-defined crystallization peaks corresponding only to the tetragonal phase (even present as practically the only phase at 600 °C). This result contrasts with that registered for ZrO_2 prepared in the absence of H_2O_2 (Figures 2 and 3). The monoclinic phase clearly appears in ZHP*n* samples calcined at 800 °C (in a proportion of 70−80%) and as the only phase for the sample calcined at 1000 °C. It is also observed that the tetragonal phase seems to be slightly dependent on the molar ratio of H_2O_2. In this way, for samples calcined at 600 °C, X_M is higher for zirconia prepared in a 1:1 molar ratio of H_2O_2, i.e., ZHP1 samples.

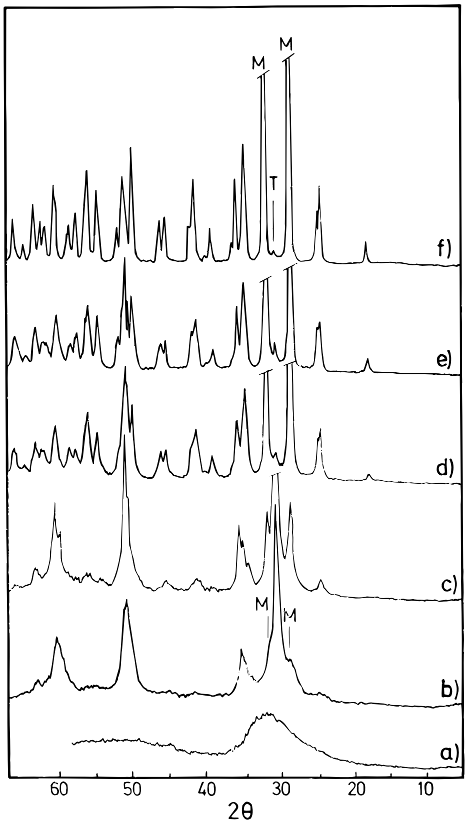


Figure 2. X-ray diffraction patterns for ZrO_2 calcined at temperatures of (a) 300, (b) 350, (c) 400, (d) 600, (e) 675, and (f) 875 °C for 4 h.

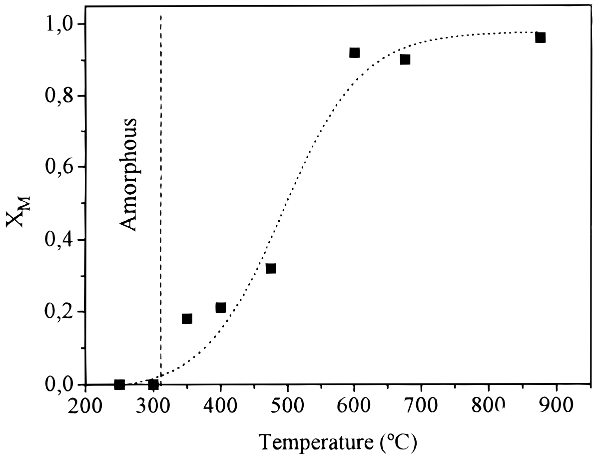


Figure 3. Variation of the monoclinic molar fraction, X_M, for ZrO_2 calcined at different temperatures for 4 h.

For sulfated samples (Figure 5), a significant delay in the crystallization process is observed at first. Sulfated samples calcined at 400 °C already showed

---

(20) Navio, J. A.; Colón, G.; Macias, M.; Campelo, J. M.; Romero, A. A.; Marinas, J. M. *J. Catal.* **1996**, *161*, 605.

(21) Mercera, P. D. L.; van Ommen, J. G.; Doesburg, E. B. M.; Buggraf, A. J.; Ross, J. R. H. *Appl. Catal.* **1990**, *57*, 127.

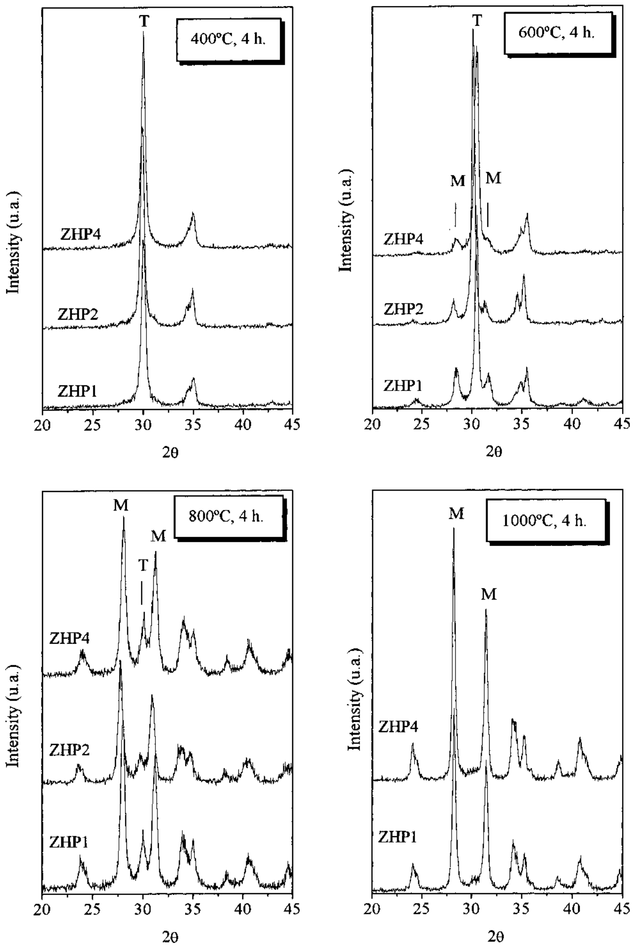


Figure 4. X-ray diffraction patterns for ZHP*n* samples calcined at indicated temperature for 4 h.

amorphous XRD patterns, behavior very different from that exhibited by the nonsulfated samples (Figure 4). Calcination at 600 °C produces the crystallization of this set of samples only in the tetragonal phase, similar to the nonsulfated ZHP*n* specimens calcined at 400 °C. The monoclinic phase does not appear predominant before a temperature of 800 °C for which X_M are about 40−60%. Again, the lowest X_M values are shown for the sample prepared with higher H_2O_2 molar ratio (ZHP4/S, X_M = 38% at 800 °C).

Table 2 shows the calculated X_M values for ZHP*n* and ZHP*n*/S samples calcined at different temperatures. These results could be explained on the basis of the structure of precursors obtained after the precipitation step. The precipitation with aqueous ammonia solution would produce a gel composed mainly of hydroxylated units of Zr^{4+} cations (α-type). This polycation unit would lead upon calcination to a monoclinic ZrO_2, as has been previously reported.[1,9] In our case, the presence of hydrogen peroxide in the starting solution would generate predominantly polycations with a high number of peroxidic bonds that after drying remain as oxo groups in the polycation unit, in other words the γ-type. This precursor structure leads after calcination to the tetragonal phase, and moreover, the crystallization process takes place at a lower temperature due to the high lability of these peroxidic groups. Thus, the tetragonal phase is achieved at a lower temperature and as the only phase, in contrast with the mixed phases found in the zirconia specimens obtained by the same procedure but in the absence of hydrogen peroxide.

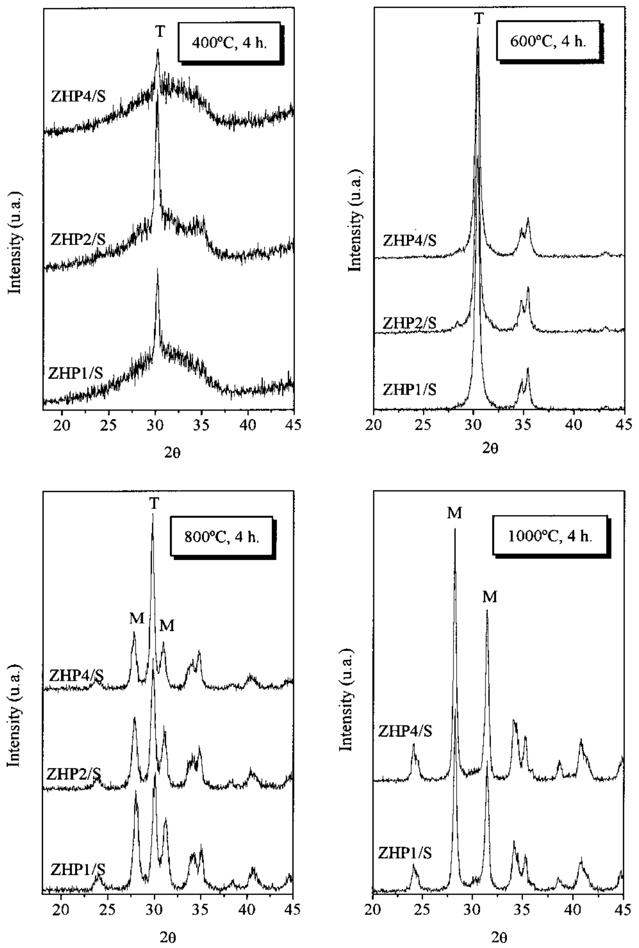


Figure 5. X-ray diffraction patterns for ZHP*n*/S samples calcined at indicated temperature for 4 h.

Table 2. Monoclinic Molar Fraction, X_M, for ZHP*n* and ZHP*n*/S Samples Calcined at Several Temperatures for 4 h

	calcination temp (°C)			
samples	400	600	800	1000
ZHP1	0.0(T)	0.28	0.83	1.0
ZHP2	0.0(T)	0.15	0.71	1.0
ZHP4	0.0(T)	0.15	0.81	1.0
ZHP1/S	(T)	0.0(T)	0.59	1.0
ZHP2/S	(T)	0.0(T)	0.52	1.0
ZHP4/S	(T)	0.0(T)	0.38	1.0

With respect to the spectral features, a significant difference can also be observed for zirconia samples prepared with or without H_2O_2. Figure 6 shows the IR spectra, in the range 1800−800 cm^{-1}, for ZHP*n* samples dried at 110 °C for 12 h (Figure 6a) and the same samples calcined at 500 °C for 2 h (Figure 6b). In this range, several bands can be found which can be ascribed to OH groups of molecular water (δ_{OH} = 1630 cm^{-1}), CO_3^{2-} (v_2 = 1540 and 1300 cm^{-1}) and NH_4^+ (δ_s = 1670 cm^{-1} and δ_{as} = 1380 cm^{-1}).[22] Carbonate and ammonium ions appear adsorbed in the surface from the high alkaline medium of the preparation. While carbonate species seem to be practically eliminated after calcination at 500 °C for 2 h, the ammonium ions are not totally eliminated upon the same thermal treatment (Figure 6b). Presumably, the IR data will show peaks for both surface and bulk species; thus it is not clear if

---

[22] Nakamoto, K. In: *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley: New York, 1985.

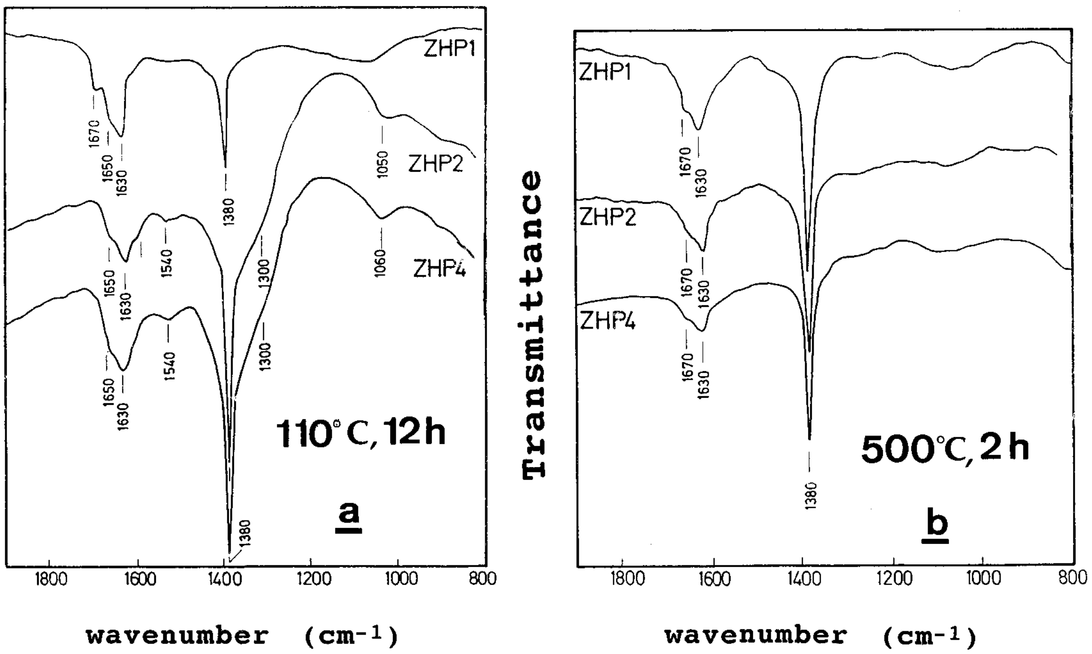


Figure 6. IR spectra for ZHP*n* samples (a) dried at 110 °C overnight and (b) calcined at 500 °C for 2 h.

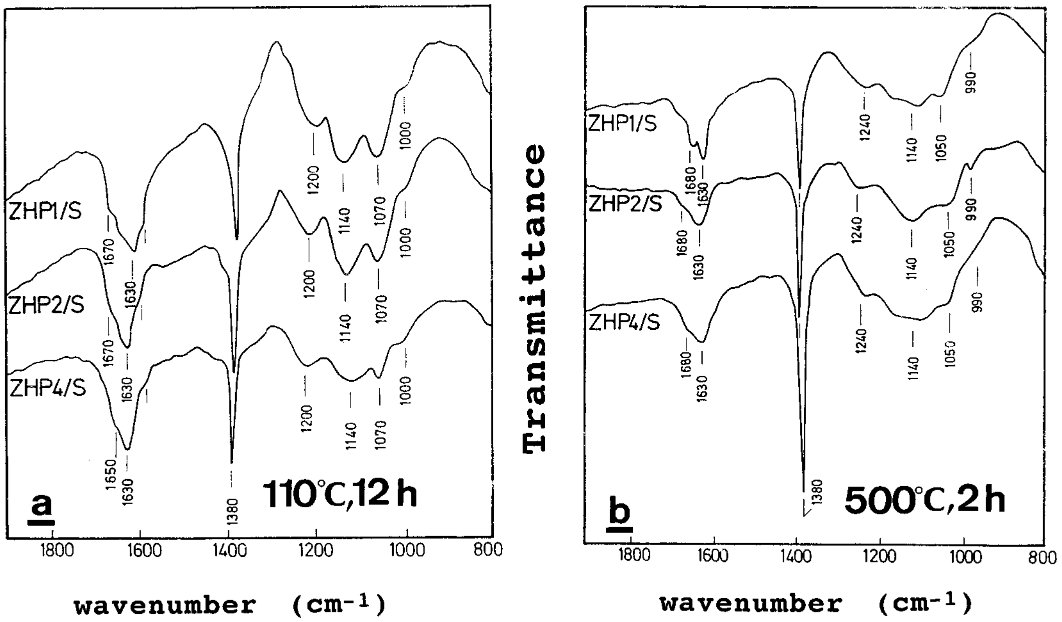


Figure 7. IR spectra for ZHP*n*/S samples (a) dried at 110 °C overnight and (b) calcined at 500 °C for 2 h.

the ammonium ion should be considered only a surface species. Zirconium hydroxide (or hydrated zirconia) adsorbs cations and anions in an aqueous solution. In an acidic solution, it adsorbs anions such as SO_4^{2-} ions, while in a basic medium, cations are preferentially absorbed.[10] The fact that the NH_4^+ ions seem to be retained even after calcination at 500 °C could indicate that this species not only is adsorbed at the surface but is also probably absorbed into the bulk matrix. It is worth noting that as the amount of H_2O_2 increase, in the preparation procedure, the intensity of the $\delta_{as}(NH_4^+)$ band (Figure 6a) seems, also, to increase, indicating that the adsorption of this cation could be related to the presence of peroxidic unions.

Sulfated series (Figure 7) also exhibited the same spectral feature, now showing the adsorbed sulfate group bands (1200, 1140, 1070, and 1000 cm^{-1}) that correspond to the S−O vibrations.[22−24] The vibration band corresponding to S=O bond, which is expected at around 1400 cm^{-1}, is probably overlapped by the δ_{as}-(NH_4^+) band. It can be observed that for sulfated samples the band ascribed to NH_4^+ seems to have lower intensities compared to those observed for the nonsulfated ones. It could be assumed that the NH_4^+ ions adsorb at the surface by a displacement of the peroxidic groups. In addition, the sulfation process produces a disminution of these cations in this case by acid−base displacement.

Finally, by comparing the IR spectra of ZHP*n* and ZHP*n*/S samples with the spectra of ZrO_2 (Figure 8), it can be said that for the latter, the bands ascribed to

---

(23) Bensitel, M.; Saur, O.; Lavalley, J. C.; Mabilon, G. *Mater. Chem. Phys.* **1987**, *17*, 249.

(24) Bensitel, M.; Saur, O.; Lavalley, J. C.; Barrow, B. A. *Mater. Chem. Phys.* **1988**, *19*, 147.

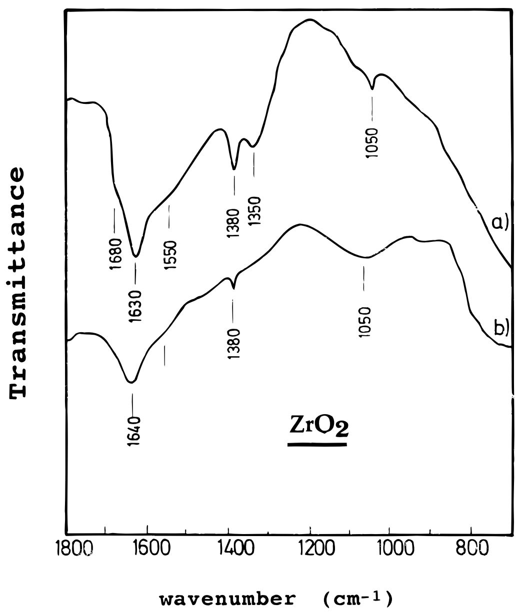


Figure 8. IR spectra for ZrO_2 (a) dried at 110 °C overnight and (b) calcined at 500 °C for 2 h.

NH_4^+ ions appear as weak bands. Thus, a relationship can be deduced between H_2O_2 presence (i.e., peroxidic groups) and NH_4^+ adsorption in the ZHP*n* samples prepared when hydrogen peroxide was used.

Conclusions

Preparation of ZrO_2 by alkaline hydrolysis of $ZrOCl_2\cdot 8H_2O$ leads to an amorphous oxohydroxide precursor that upon calcination at temperatures higher than 350 °C produces a crystalline ZrO_2 sample with mixed crystallographic phases (monoclinic and tetragonal).

Preparation of this material, by the same precipitation procedure, but adding different molar ratios of hydrogen peroxide produces amorphous precursors (ZHP*n*) developing, mainly, the tetragonal crystal phase at the same calcination temperatures. The molar fraction of the phases seems to be dependent on the H_2O_2 molar ratio, thus indicating a direct relationship of this parameter with the crystallization behavior.

At the same time, preparation with H_2O_2 seems to retain NH_4^+ from the alkaline medium, even after calcination at 500 °C for 2 h. The sulfation process of these ZHP*n* samples also modifies the structural properties; in this case, the crystallization process is delayed at higher temperatures, but with the same crystallographic features of the nonsulfated series, stabilizing the tetragonal phase up to the temperature of 800 °C.

Acknowledgment. The authors acknowledge the subsidy received from the “Dirección General de Investigación Científica y Técnica” (DGICYT-Spain) Project PB93-0917, for supporting part of this work. We also gratefully acknowledge the “Consejeria de Educación y Ciencia/Junta de Andalucia” (Spain). J.A.N. thanks the NATO Science Committee for a Linkage Grant (HTECH.LG 960967).

CM960625P