CHARACTERIZATION AND CATALYTIC ACTIVITY OF ZIRCONIUM DIOXIDE PREPARED BY SOL-GEL

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Abstract — **Zirconia samples prepared from Zr(*n*-OC_3H_7)$_4$ and $ZrOCl_2$ were characterized by XRD, BET surface area, TG-DTA, TEM/SEM, FTIR, and D_2O exchange. Oxides obtained from the alkoxide contain two types of hydroxyl groups at 3704 and 3597 cm^{-1}, which do not exchange with D_2O. Those obtained from $ZrOCl_2$ produced three types of hydroxyl groups at 3774, 3733 and 3671 cm^{-1}, which do exchange with D_2O. Surface acidity was determined by FTIR of adsorbed lutidine. Only Lewis acid sites were found on samples from $ZrOCl_2$ hydrolysis. FTIR spectra of calcined samples exhibited strong absorption bands in the 1800 to 1000 cm^{-1} region, which are ascribed to various types of carbonate and bicarbonate species. These ones are strongly adsorbed on the surface oxide and they are removed only after 3 hours at 600 ºC in stream of H_2. Samples derive from the alkoxide precursor restore the original carbonate species after exposure to O_2 at 600ºC. Catalytic activity for *i*-propanol dehydration/dehydrogenation showed the absence of basic centers and an intermediate dehydration activity between that of silica and alumina.**

Key words — **Zirconium oxide, zirconia, acidity, FTIR, 2,6-lutidine.**

I. INTRODUCTION

Zirconia is a very important ceramic material with growing application to heterogeneous catalysis both as active material and support. For example, Miller and Grassian (1995) have tested the decomposition of NO on zirconia nanoparticles and suggested that it occurs in Lewis acid sites. Yokoyama *et al.,* 1992) have found a correlation between the surface acid-base properties and the activity to reduce carboxylic acid to aldehydes. Various authors (Nakano *et al.*, 1979; Ferino *et al.*, 2000; He and Ekerdt, 1984a and He and Ekerdt, 1984b) have reported on the catalytic activity of zirconia to the selective dehydration of secondary alcohols to terminal alkenes as well as to the hydrogenation of CO to isobutane.

Zirconium oxide can be prepared by the sol gel technique (Brinker and Scherer, 1990) using inorganic precursors, like $ZrOCl_2$, or metalorganic ones, as zirconium alkoxides. The aim of this work was the characterization of zirconia pure samples, prepared from $ZrOCl_2$ or Zr(n-OPr)$_4$, as well as to establish a correlation between superficial properties and preparation methods.

II. EXPERIMENTAL

A. Sample preparation

A 0.01 *M* aqueous solution of $ZrOCl_2.8H_2O$ was neutralized by slowly adding 1*M* solution of NH_4OH to the gel formation. The gel was washed with absolute ethanol to negative chloride test.

0.1 *M* solutions of Zr(n-OC_3H_7)$_4$ in absolute ethanol were mixed with 0.1 *M* water/ethanol solutions (Davies *et al.,* 1995 and 2000). A white fine precipitate appeared immediately after mixing both solutions. The molar ratio water/alkoxide, *h*, was fixed at 2 and 16. Molar ratio equal to 2 is considered the stoichiometric one in accord to the following equation (Brinker and Scherer, 1990):

$$Zr(\text{-}OPr)_4 + 2\ H_2O \longrightarrow ZrO_2 + 4\ PrOH$$

For both preparations, solvent was removed at 60ºC in a vacuum rotary evaporator and solids were dried overnight at 120ºC. Finally, samples were calcined at least for 3 hours at 600ºC

B. Characterization methods

Self-supporting wafers (7 mm diameter) for FTIR analysis were obtained from dried samples and then calcined up to 600ºC for three hours. FTIR studies were performed in a quartz cell which had KRS5 windows. The cell, connected to a vacuum system (10^{-2} Torr), allows *in situ* thermal treatment of samples from room temperature up to 600ºC. All FTIR spectra were obtained at room temperature with a Bruker IFS 88 (4 cm^{-1} resolution).

After evacuation at 300°C and cooling down to room temperature, D_2O vapor was admitted into the cell followed by taking the FTIR spectra at increasing evacuation temperatures. Acidity studies were performed using 2,6-dimethylpyridine (2,6-lutidine) as probe molecule following a similar procedure to that with D_2O. Treatments with a stream of H_2 and O_2 up to 600°C were followed to analyze the evolution of carbonates.

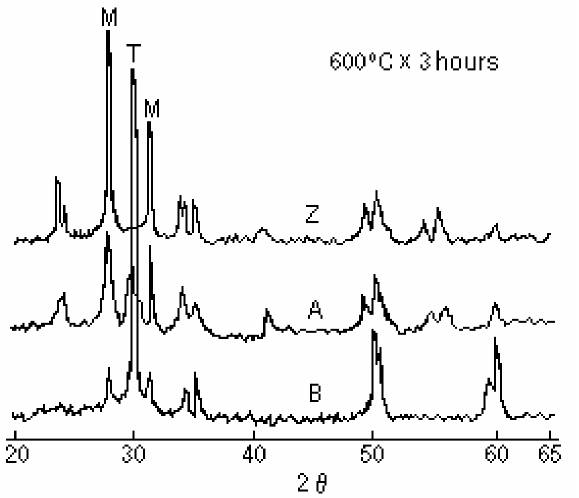

Figure 1: XRD patterns of samples A, B and Z calcined at 600ºC for 3 h. M = monoclinic phase. T = tetragonal phase.

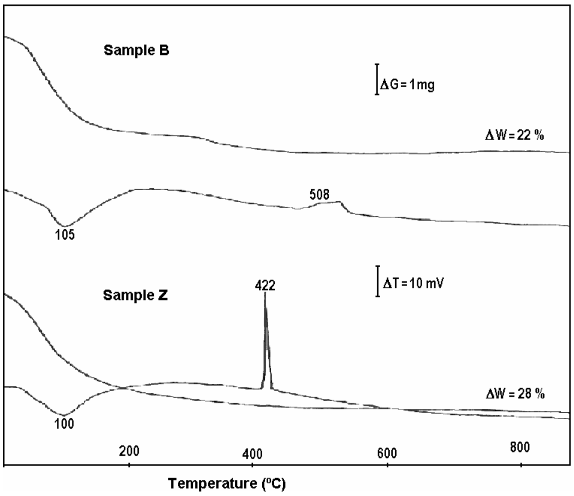

Figure 2: TG/DTA profiles for samples A120 and B120. Thermal analysis data were collected in the 20-900ºC range under oxygen flow at 10º/min. Z120 profile is similar to that of sample A120.

Crystal structure of the samples was determined by X-ray diffraction with a Rigaku Denki D-Max IIC diffractometer using CuK$_\alpha$ for 2θ between 20° and 65º. Morphology was assessed by TEM/SEM through conventional techniques. BET surface area was determined by adsorption of N_2. Thermogravimetric analysis (TG-DTA) was performed in a Rigaku Denki analyzer in air from room temperature up to 900ºC at a heating rate of 10º/minute.

Catalytic test were carried out in a 5 mm internal diameter continuous flow fixed bed Pyrex reactor. N_2 (99,998%) was used as gas carrier at 150/300 mL/min. Total pressure was slightly higher over the local atmospheric one (660 Torr). The amount of catalyst loaded and the temperature were selected in order to obtain comparable conversions. The absence of diffusive effects was verified in each run. The stream of N_2 was saturated with the alcohol through a thermostatized vaporizer. The alcohol partial pressure was maintained at 38 Torr (5,8% molar) in all experiments. Alumina (Aldrich, 58Å, 155 m^2/g) and silice (Davison G62, 74Å, 300 m^2/g) without any other treatments were used with comparative purposes.

III. RESULTS AND DISCUSSION

A. General

Table 1 shows the main structural characteristics of zirconia samples. Only those prepared from a stoichiometric water/alkoxide ratio (*h* = 2) have controlled morphology (sample B). The mean diameter of spheres (about 1μm), determined from TEM experiments, was employed to estimate the surface area of B600 samples.

The unshaped samples A120 and Z120 have considerable surface area but it is strongly diminished after calcining at 600ºC.

All dried samples (120°C) were amorphous to X-ray diffraction. Monoclinic phase was the main one for all 600ºC-long time calcined samples.

The monoclinic to tetragonal ratio depends on the morphology, the previous thermal treatment and the time that the sample was maintained at the final temperature. So, for sample formed by spherical particles (B120) after 3 hours calcination at 600ºC, tetragonal phase is the 74% of the total crystalline phases (Fig. 1). After 48 hours at this temperature the monoclinic phase increases up to 86%. Sample A120 shows the monoclinic phase as the main crystalline phase after 3 hours calcination. For the Z600 sample the monoclinic phase was the only one detected after 3 hours at 600°C (Fig.1).

TG-DTA profiles show a distinctive behavior for each sample (Fig. 2). The total weight loss in the temperature range 20 - 900ºC is about 22% for B120 and 28% for

Table 1: main structural characteristics of zirconia pure samples

Sample	Precursor	*h* (1)	Morphology (2)	Thermal Treatment, °C	Crystalinity (3)	S_{BET} (4)
A120	Zr-$(OC_3H_7)_4$	16	unshaped	120	amorphous	42
A600	Zr-$(OC_3H_7)_4$	16	unshaped	600	M (+ T)	8
B120	Zr-$(OC_3H_7)_4$	2	spheres	120	amorphous	--
B600	Zr-$(OC_3H_7)_4$	2	spheres	600	M (+ T)	<2
Z120	$ZrOCl_2$	--	unshaped	120	amorphous	194
Z600	$ZrOCl_2$	--	unshaped	600	M (+ T)	37

1. ***h*** = mole ratio $H_2O/Zr(OC_3H_7)_4$. **2**. By TEM/SEM. **3**. By XRD, M = monoclinic phase, T = tetragonal phase. **4**. BET area in m^2/g by N_2 adsorption after evacuation at 200°C.

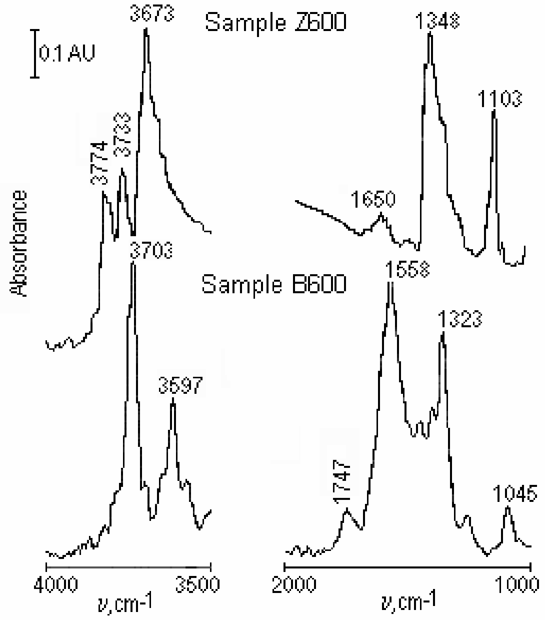

Figure 3: FTIR spectra showing the hydroxyl and carbonate-regions of sample Z600 and B600 after outgassing (P = 25 μHg) at 300 ºC for 1 h. FTIR spectrum of sample A600 is similar to that of B600.

Z120. The total weight loss is related to the removal of solvent and also to the combustion of residual organics (Ferino *et al.*, 2000). Between 500 and 540ºC, DTA curve for sample B120 showed a complex and exothermic transformation, while a "glow" exothermic peak was observed at 425 ºC for sample Z120. This strong exothermic peak has been assigned to a sudden transition from amorphous to monoclinic phase in zirconia samples (Mercera *et al.*, 1990), in agreement with XRD analysis showing that sample Z (Fig. 1) crystallizes into monoclinic phase after three hours at 600ºC. On the other hand, the transformation at 500-540°C observed in the B120 sample could be assigned to a slow transition from the amorphous to tetragonal and then to the monoclinic phase also in agreement with the XRD results showing that tetragonal is the first crystalline phase after treatment at 600ºC for 3 hours (Fig. 1).

B. Thermal treatment in vacuum

Two hydroxyl bands (3703 and 3597 cm^{-1}) were observed on FTIR spectra for samples A600 and B600 after vacuum at 300°C, while three bands were observed for sample Z600 (Fig. 3).

For sample Z600 the absorption bands corresponding to hydroxyl groups agreed very well with values reported on bibliography. They were assigned to isolated and bridged hydroxyl groups (3774 and 3673 cm^{-1}) belonging to the monoclinic phase and to isolated monocoordinated HO groups (3733 cm^{-1}) of the tetragonal phase (Guglielminotti, 1990; Hertl, 1989, Agron *et al.*, 1975, Erkelens *et al.*, 1972). However, there is no agreement with reported data respect to the band at 3703 cm^{-1} that appears on the A600 and B600 samples. The absorption band at 3597 cm^{-1} could be assigned to hydroxyl group of a bicarbonate specie (A600 and B600).

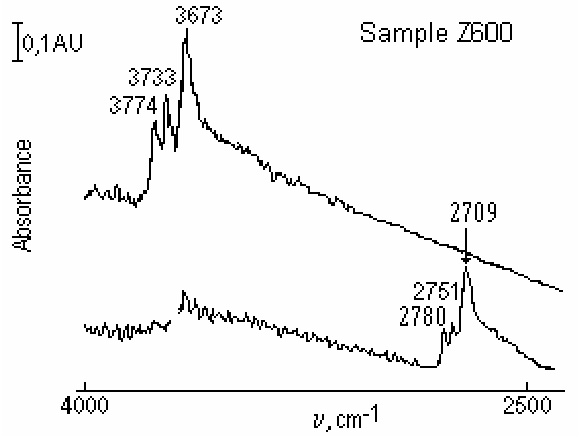

Figure 4: FTIR spectra for sample Z600 showing the D_2O exchange of OH-groups. The OD- bands were fully observed after outgassed (P = 20 μHg) at 200 ºC for 30 min. Samples A600 and B600 do not show D_2O exchange.

The bands in the 2000 to 1000 cm^{-1} region were assigned to various types of carbonate species (Fig. 3, right). The profiles of these bands were different depending on the preparation route. For samples derived from alkoxide precursors, FTIR spectra always showed a very intense and sharp band at 2340 cm^{-1}. This band was assigned to CO_2 trapped inside the bulk structure of the oxide. Absorption bands due to carbonate species along with CO_2 are missing from the FTIR spectra after H_2 treatment (see **E** section below).

C. D_2O Exchange

The nature and reactivity of hydroxyl groups were studied by D_2O exchange. Fig. 4 shows the FTIR spectra of Z600 sample between 4000 and 2500 cm^{-1} after deuterium oxide exchange. It is observed that the three hydroxyl bands at 3774, 3733 and 3673 cm^{-1} have changed to 2780, 2751 and 2709 cm^{-1}.

The wave number ratio OH/OD is 1.36, value that is in agreement with the expected one for isotopic substitution (Bensitel *et al.,* 1987). Thus, these hydroxyl groups are exposed and available on the oxide surface. On the other hand, hydroxyl bands at 3703 and 3597 cm^{-1} observed on FTIR spectra of A600 and B600 samples did not exchange with D_2O at any temperature up to 300ºC indicating that these OH-groups are occluded inside the oxide structure.

D. Superficial acidity

Surface acid sites were studied using 2,6- dimethylpyridine (2,6-lutidine) as probe molecule due to its enhanced basicity (pK_b 7.4) compared to pyridine (pK_b 8.8). Consequently the former can interacts with Brönsted acid sites weaker than those detected with pyridine (Corma *et al.,* 1984). As a result of hydrogen interaction between superficial OH-groups and 2,6-lutidine hydroxyl groups were not longer observed on FTIR spec-

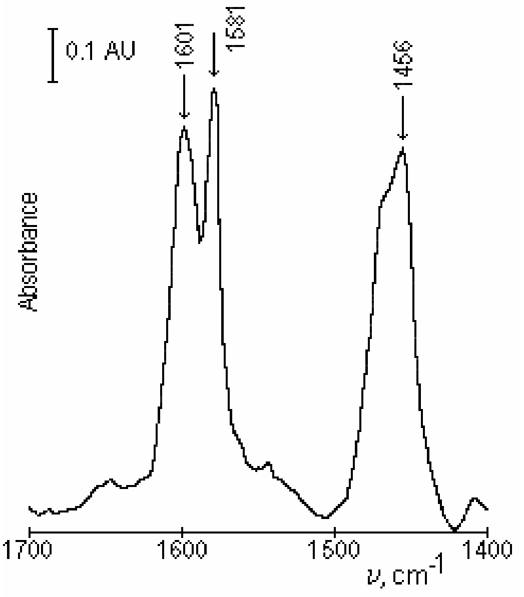

Figure 5: FTIR spectrum of 2,6-lutidine adsorption on sample Z600 after outgassing (P = 20 μHg) at 50ºC for 30 min.

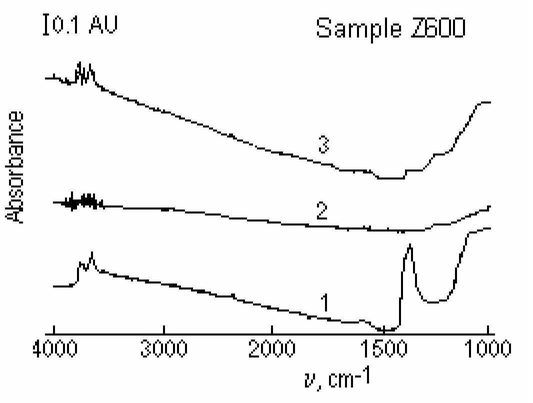

Figure 6: FTIR spectra of self-supporting wafers of sample Z600. (**1**) outgassed at 550ºC for 20 min under 20 μHg. (**2**) After exposure to H_2 stream at 600ºC for 3 h and followed by outgassing at rt for 5 h. (**3**) after exposure to O_2 stream at 600ºC for 3 h and followed by outgassing at rt for 1 h.

tra of Z600 sample after lutidine adsorption. The infrared bands at 1601, 1581 and 1456 cm^{-1} shown in Fig. 5 are associated with lutidine adsorbed on Lewis acid sites. These bands disappeared under vacuum at 100ºC demonstrating a very weak interaction between the probe molecule and Lewis acid sites. The interaction with 2,6-lutidine also changed the shape and position of carbonate bands not being restored after evacuation at 100ºC.

The FTIR spectra of lutidine adsorption on A600 and B600 samples revealed the absence of interaction between the probe molecule and hydroxyl groups, although a new band is developed at 3627 cm^{-1}. Therefore the hydroxyl groups at 3703 and 3597 cm^{-1} are not accessible for reaction with lutidine. Furthermore, after the lutidine adsorption, the spectra did not show any bands in the region from 1800 to 1000 cm^{-1}, behavior probably related to the very low surface areas of these samples.

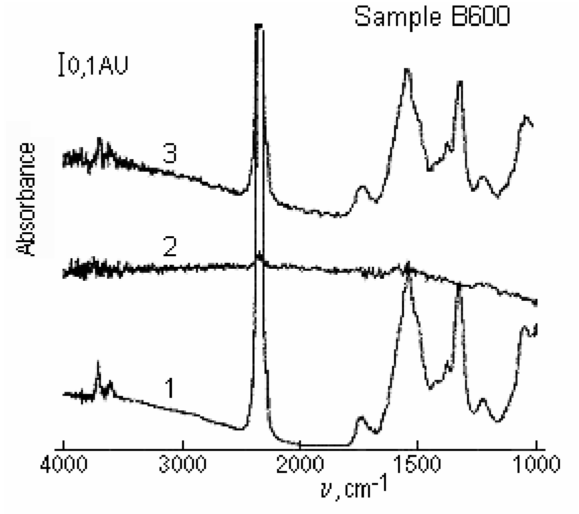

Figure 7: FTIR spectra of self-supporting wafers of sample B600. (**1**) outgassed at 550ºC for 20 min under 20 μHg. (**2**) After exposure to H_2 stream at 600ºC for 3 h and followed by outgassing at rt for 5 h. (**3**) after exposure to O_2 stream at 600ºC for 3 h and followed by outgassing at rt for 1 h. Sample A600 shows a similar behavior.

Table 2

Sample	S_{BET}	T/°C	E_a	%S
SiO_2	300	387	20,43	93
A600	34	333	27,93	100
Z600	8	322	24,13	>99
Al_2O_3	150	242	25,72	100

Sup. BET = m^2/g
T needed to reach $r = 1.10^{-6}$ mole alkene /h.m^2.
E_a = Kcal/mol
%S = selectivity to alkene

E. Treatment with H_2 and O_2

All the absorption bands in the 4000 to 1000 cm^{-1} range were missing after treatment in a stream of H_2 up to 600 ºC indicating that hydroxyl and carbonate groups were fully destroyed. After exposure to O_2, sample Z600 recovered the bands due to hydroxyl groups but no the bands in the region between 1800 to 1000 cm^{-1} corresponding to carbonate species (Fig. 6). So hydroxyl groups are independent from the carbonate ones as it was already demonstrated after D_2O exchange and 2,6-lutidine adsorption.

On the other hand, after exposure to O_2 at 600ºC samples B600 and A600 restored the original spectra in the whole range between 4000 to 1000 cm^{-1} showing evidence that hydroxyl and carbonate groups are closely related (Fig. 7). This behavior clearly demonstrates that carbonate groups are only reduced to carbon but no removed so they reoxidize after O_2 exposure. Moreover the hydroxyl band at 3597 cm^{-1} could be assigned to

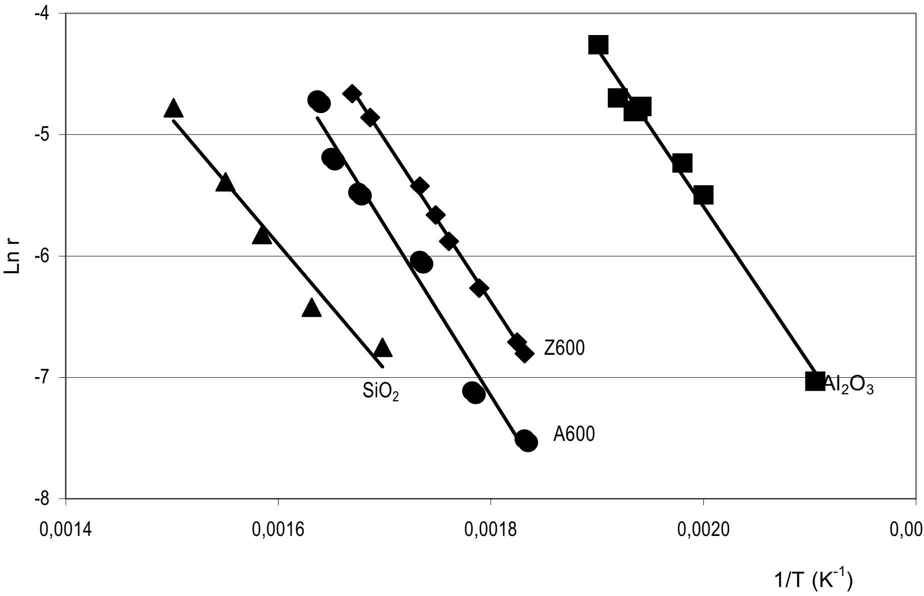

Figure 8: Arrhenius plot for the dehydration of *i*-propanol for A600 and Z600 samples. r = mole alkene/h.m^2 at 8% total conversion.

bicarbonate species trapped inside the bulk structure of the oxide. In this way, the 3597 cm^{-1} band can not exchange with D_2O as it was mention on section C above.

F. Catalytic Activity

Fig. 8 shows the Arrhenius plot of the *i*-propanol dehydration rate for A600 and Z600 samples and

also for two well-known materials, SiO_2 and Al_2O_3.The reaction rates values are given per unit surface area so that they are comparable.

Table 2 shows the surface area of each sample, the temperature needed for reaching a reaction rate of 10^{-6} mol alkene /h m^2 and the selectivity to alkene at 8% alcohol conversion. This value can be considered as indicative of the reactivity and acidity of these materials (Franklin *et al.,* 1991).

From the values shown in Fig. 8 and in Table 2, it is concluded that both materials (A600 and Z600) posses similar catalytic activity. Moreover, the selectivity to alkenes indicates the absence of basic sites with capacity to produce carbonyl compounds. In all the experiments it was observed a selectivity to alkene higher than 99%. SiO_2 is the only material that shows, at higher temperatures, a remarkable conversion to carbonyl products.

It is important to realize that the zirconia samples show specific activities (moles of alcohol converted/hour m^2) between those observed for silica and alumina.

On the contrary to the behavior of alumina, whose activity is attributed to Brönsted acid sites, the catalytic activity of zirconia is related to Lewis acid sites.

IV. CONCLUSIONS

Both precursors (alkoxide or inorganic salt) lead to materials with different morphologic and structural characteristics. For the alkoxide route, the hydrolysis ratio, *h*, defines the particle morphology. On the other hand, samples from the inorganic salt $ZrOCl_2$ show three types of OH groups attributed to the coexistence of monoclinic and tetragonal phases. Samples from alkoxide show only two OH bands at 3597 and 3703 cm^{-1}, which do not exchange with D_2O, being the 3597 cm^{-1} band assigned to bicarbonate species.

Although all the materials posses carbonate species shown by FTIR, the origin and structure of these species are diverse. For the alkoxide route, the carbonate species come from the decomposition of alkoxide precursor in air along with the formation of CO_2. Both carbonate species and CO_2 are occluded inside the bulk structure of zirconia. For the inorganic route, these species are located on the surface of the oxide. However, both samples show a similar acidity respect to i-propanol dehydration, showing a catalytic activity between that of alumina and silica.

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