

NANO ZIRCONIA AND SULFATED ZIRCONIA FROM AMMONIA ZIRCONIUM CARBONATE

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Abstract. A novel method for producing either nanosized zirconia or sulfated zirconia from ammonia zirconia carbonate, an inexpensive chemicals commodity, is described. Thermal, morphological and crystallographic characterization vs the particle size and phase were determined, sulfation efficiency of the process was increased.

1. INTRODUCTION

About 25 years ago, reports on sulfated zirconia and related metal oxides showing a highly remarkable strong acidity, along with studies on their high efficiency for the isomerization of alkanes, opened a new field of R&D in catalytic materials. Even since, several groups around the world have investigated the structure and properties of these superacid materials [1-12]. In particular, considerable attention has been paid to the reason for their superacidity [11-19] and the effect of this rather unusual property on applications other than catalysis, including thermoluminescent devices [20].

In this regard, zirconia, when modified with anions such as sulfate, forms a highly acidic or superacidic catalyst exhibiting superior catalytic activity in many reactions of practical and scientific interest [8-11]. Generally speaking, sulfated zirconia is a crystalline solid acid which presents monoclinic and tetragonal phases with a typical super acidity of -16.04 (Hammett acidity) or even higher, according to some reports. This superacidity is supposed responsible for the enhanced catalytic activity of

these materials. A variety of organic reactions that are normally catalyzed by Brønsted or Lewis acids have been shown to take place much more efficiently in the presence of sulfated oxides, especially sulfated zirconia even under milder reaction conditions, requiring shorter times and achieving with greater selectivity and improved yields. This has been observed in a number of different reactions, ranking from alkylation, condensation, esterification, transesterification, nitration to cyclization and isomerization [21-26].

Ammonia zirconium carbonate (AZC), also known in the literature as ammonium zirconyl carbonate, is an alkaline Chemicals commodity, CAS # 68309-95-5 and CAS index name Zirconate (2), bis [carbonato (2) -0] dihydroxy-diammonium, is utilized in manufacturing of zirconium compounds, manufacturing paint drier auxiliaries, pigments, various catalysts and paper sizes. One of the main industrial uses of these chemicals is in paper technology, where such ammonium zirconium carbonate solutions are extensively used for insolubilizing the starch binders used in paper coating formulations.

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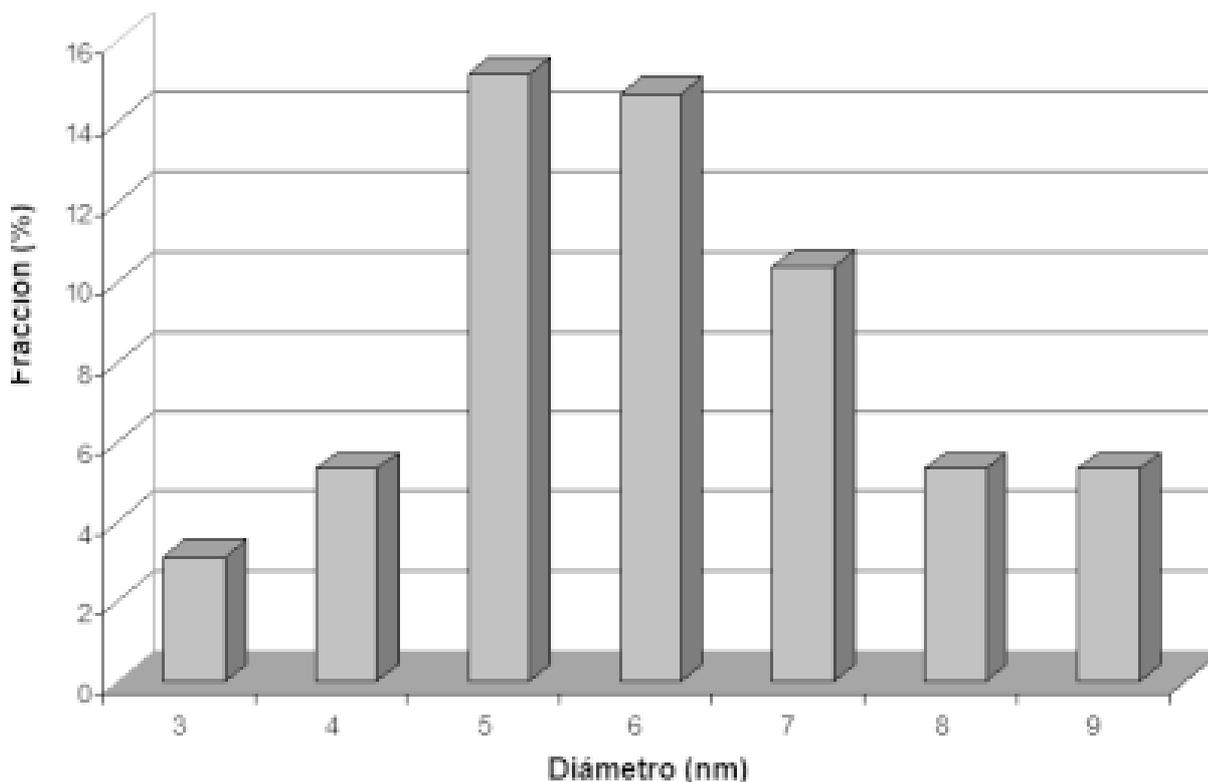


Fig. 1. Particle size distribution of ammonia zirconium carbonate sols, as obtained by dynamic light scattering.

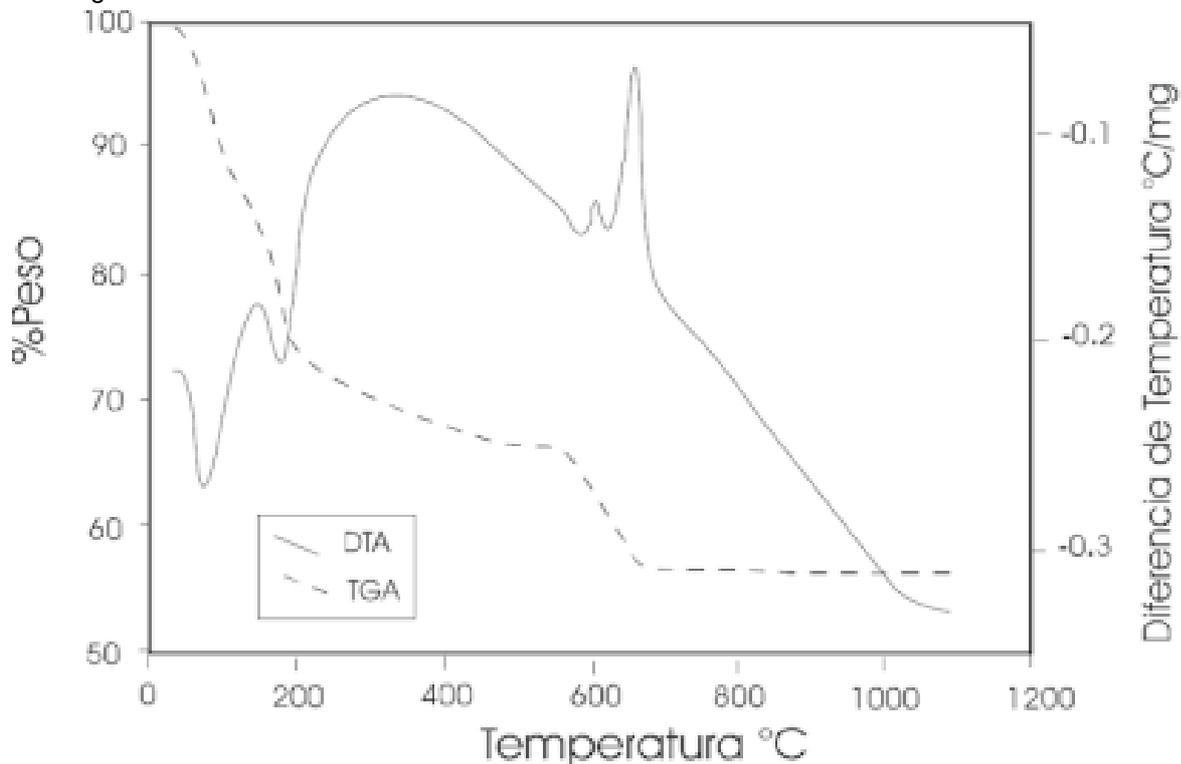


Fig. 2. TGA and DTA curves of the monolith obtained by ageing the ammonia zirconium carbonate.

To our knowledge, the use of AZC, an inexpensive chemicals commodity, for producing sulfated

zirconia a low cost and high efficiency, has not been reported, being this precisely the aim of the present

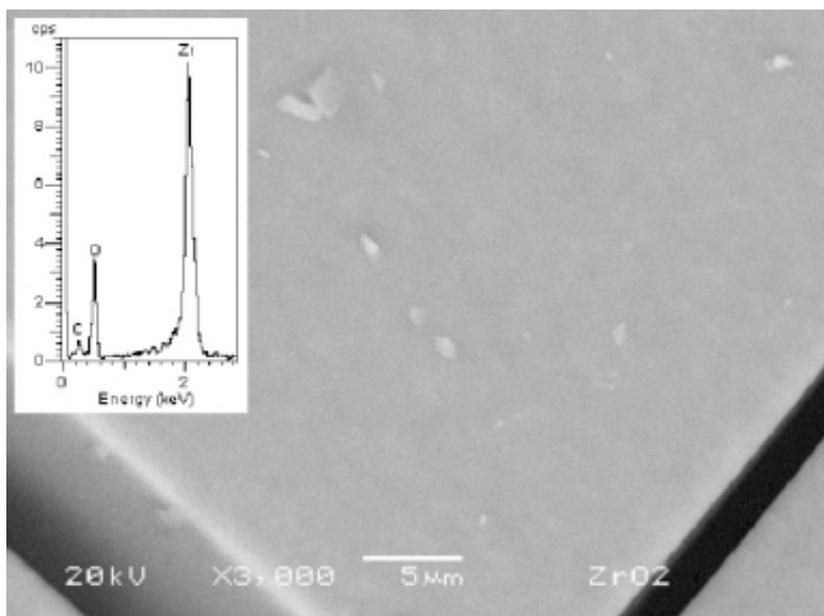
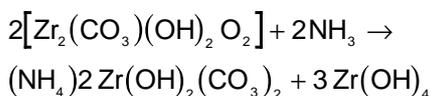


Fig. 3. SEM and EDS (inset) of the monolith obtained by ageing the ammonia zirconium carbonate. The small C signal of the EDS is due to the sample preparation for microscopy observation.

manuscript where, along with a description of the chemical route necessary, a characterization of the final product is included.

2. EXPERIMENTAL

Commercial ammonia zirconium carbonate white paste (Magnesium Electron Inc.), formed by 40% zirconium compounds and 7% CO₂ was utilized as purchased. A zirconium sol was prepared according to the following reaction [27,28]:



using ammonia (Baker) with 7.6% of NH₃.

Then, 616.9 g of zirconium carbonate were mixed with 1261.3 ml of NH₄OH 1.58 M. To support full dispersion of the paste, alumina balls were added and refluxed for 24 h, fielding an aqueous solution of ammonia zirconium carbonate (NH₄)₂Zr(OH)₂(CO₃)₂.

Particle size of the resulting sols was determined by dynamic Light scattering in a Brookhaven apparatus, model 9000.

Ageing at room temperature leads to evaporation of humidity and ammonia, thus increasing viscosity. After a week, a transparent monolith is ob-

tained, which was characterized in a TGA-DTA instrument SDT 2960 TA in the range 50 to 1100 °C. X-ray diffraction of samples calcined at 300, 450, 600, and 800 °C for 1 h was carried out in a Siemens D-5000 equipment.

Finally, the sulfated zirconia was obtained by preparing three 50 ml aqueous solutions with 0.5, 1, and 2 ml sulfuric acid, respectively, which led to CO₂ liberation and a white powder precipitates, which were filtered and dried at 60 °C for 24 h. These samples were calcined at 600 °C for 1 hour. Sulfur concentration was determined by EDS in a JEOL 5900 LV SEM. High resolution transmission electron microscopy was done in a JEOL-200CX machine.

3. RESULTS AND DISCUSSION

According to the above synthesis route, the resulting zirconia sols were nanosized, with an average diameter of 4 nm, as shown in the light scattering results summarized in Fig. 1.

Thermal analysis (DTA and TGA) of the zirconia and sulfated zirconia obtained (Fig. 2) reveals » 25% weight loss in air (TGA) along with two endothermic peaks (DTA) attributed to ammonia and water residues, in the range up to 200 °C. As for the 200 to 550 °C range, a weight loss of around

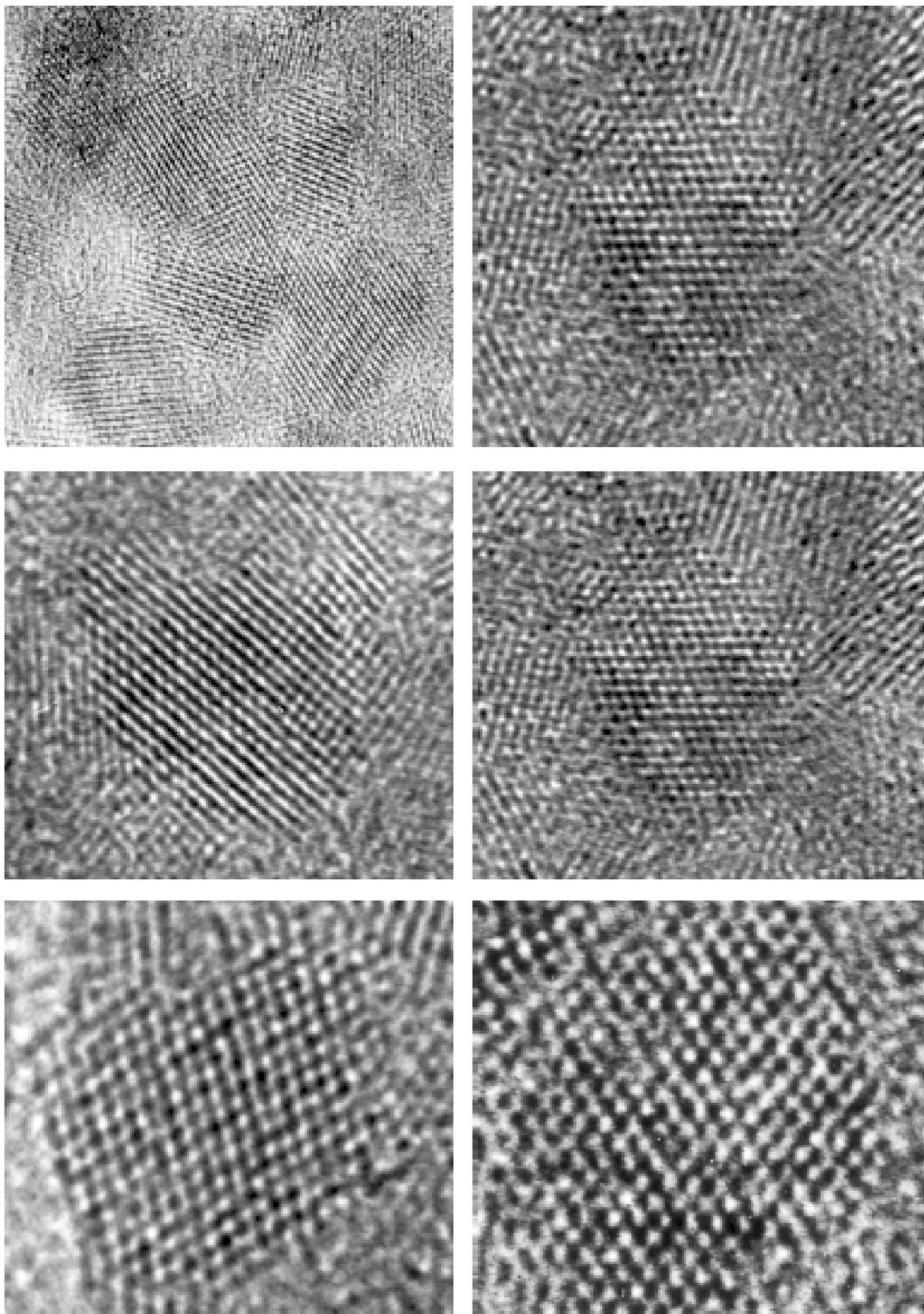


Fig. 4. Series of high resolution transmission electron microscopy of the monolith obtained by ageing the ammonia zirconium carbonate.

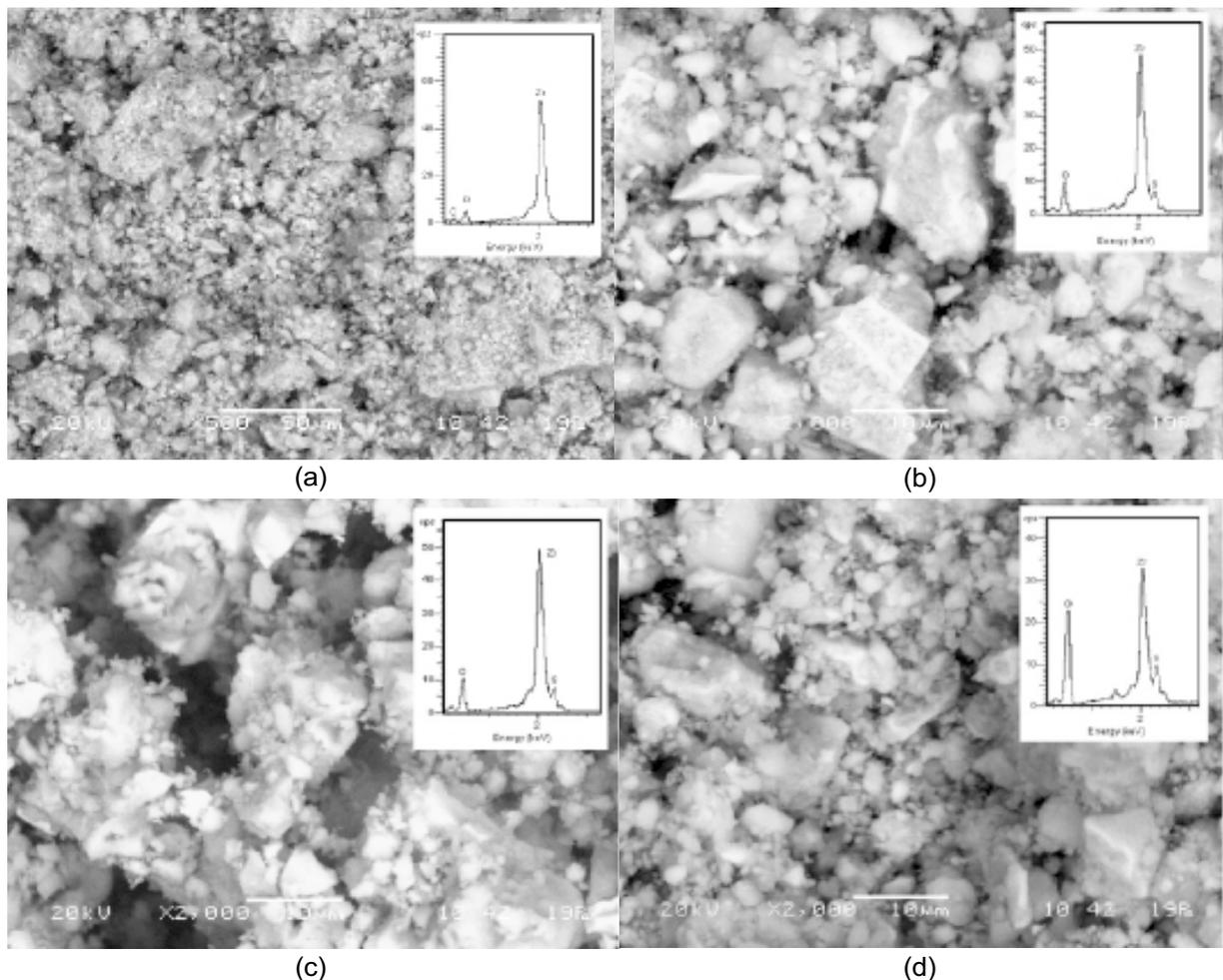


Fig. 5. Series of SEM images and EDS results (insets) of sulfated zirconia samples treated with: a) 0 ml; b) 0.5 ml; c) 1.0 ml, and d) 2.0 ml of sulfuric acid.

Table 1. S content of sulfated samples (by EDS).

Sample	S content % weight
1	0
2	1.3
3	2.4
4	4.0

10% is found, associated to a deshydrolyxation of the sample. Then, from 550 up to 650 °C there is another weight loss process, due to the elimination of CO₂, caused by the decomposition of the carbonate. This is associated to a exothermal peak

at 650 °C. Finally, the formation of the tetragonal phase is revealed through an exothermal peak at 600 °C.

As for the morphology of the monolith, the SEM image of Fig. 3 reveals a highly homogeneous, crack-free material composed only of Zr and O, as shown in the EDS inset. High resolution electron microscopy shows nanocrystals, ranging 5 to 7 nm forming the monolith (Fig. 4).

As for the sulfation, the series of spectra and SEM images of Fig. 5 summarizes the results of treating the zirconia samples with 0, 0.5, 1.0 and 2.0 ml of H₂SO₄, as described above. Table 1 shows the S content as measured by EDS, showing that, in fact, the sulfation can be controlled in this process. It is also interesting to notice that the sulfation produces agglomeration of the original nanoparticles.

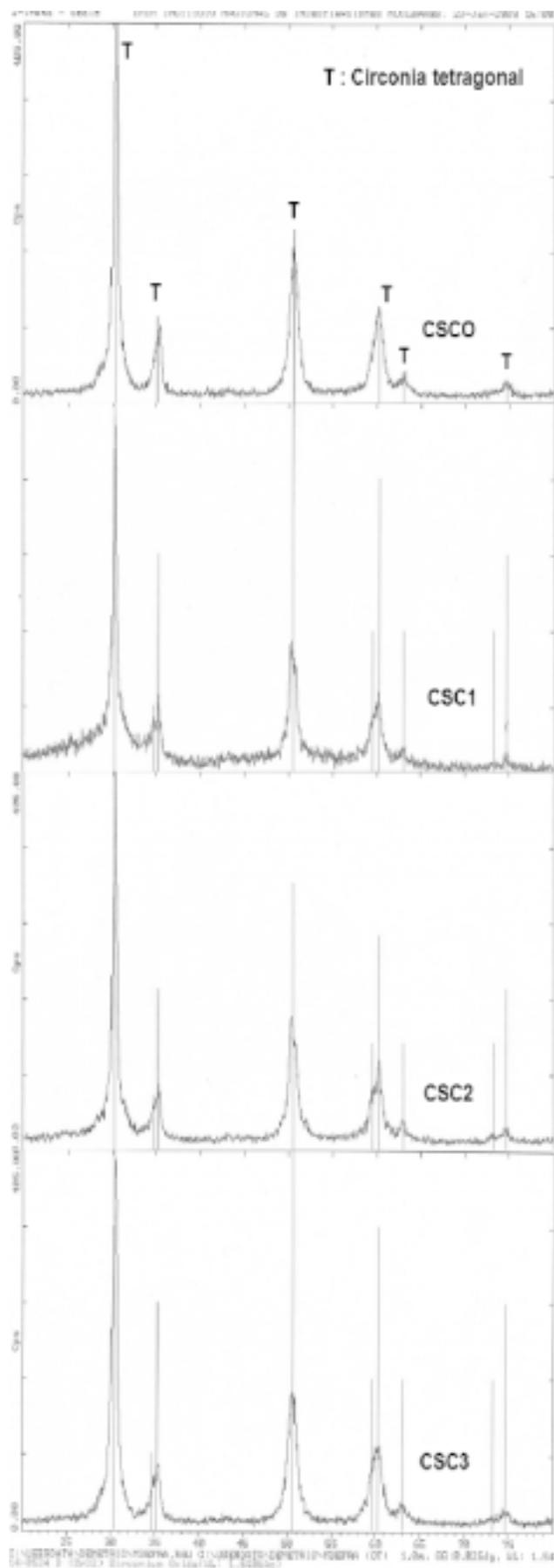


Fig. 6. Series of XRD patterns of sulfated zirconia samples, annealed at 600 °C for 1 hour : a) 0 ml; b) 0.5 ml; c) 1.0 ml, and d) 2.0 ml of sulfuric acid.

The X-ray diffraction results show an interesting effect: as opposed to pure zirconia, where annealing is known to change the crystalline structure from amorphous to monoclinic and tetragonal [18-24], the sulfated samples always keep the tetragonal phase, as shown in the series of XRD patterns of Fig. 6, corresponding to the sulfated zirconia, with different S content, treated at 600 °C for 1 hour.

4. CONCLUSIONS

An alternative method for producing both pure zirconia and sulfated zirconia from ammonia zirconium carbonate, a commodity Chemicals widely employed in the paper industry, was presented. The results show the feasibility of producing nanosized zirconia and/or sulfated zirconia, allowing to control both size and S control, in either case. The sulfated zirconia presented the tetragonal phase, as revealed by X-ray diffraction, which was stable even after annealing. Luminescent and catalytic behavior will be reported separately.

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