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Morphology and structure of zirconia-ceria based nanopowders synthesised by nitrates-EDTA and nitrates-TRIS gel-combustion routes

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Abstract

Gel-combustion syntheses (GCPs) employing different fuels are widely recognized in the literature because of their versatility, low cost and experimental flexibility. Besides, they allow to obtain a large amount of a pure, homogeneous nanopowder in a single batch process.

In a previous work the authors reported new GCPs for zirconia-ceria nanopowders, syntheses based on nitrates-EDTA and nitrates-TRIS and preliminary results of morphology and structures of the different, obtained powders calcined at selected temperatures. In this article, new results about morphological and structural characterization of nanopowders obtained by fuel-rich and stoichiometric, nitrates-EDTA and nitrates-TRIS GCPs, mainly calcined at 600°C/2 h, are informed. The characterizations were performed by SEM, TEM, DRX and S_{BET} techniques.

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By XRD, the expected retention of the metastable, tetragonal phase was established in ZrO₂-rich, calcined nanopowders (ZrO₂-15mol%CeO₂), meanwhile, in CeO₂-rich, calcined nanopowders (ZrO₂-90mol%CeO₂) the usually expected, thermodynamically stable, cubic phase was obtained.

By SEM, typical agglomerates of variable morphology were observed, depending on the GCP/composition choice. By TEM the detailed nanostructure of the nanocrystallites aggregation was observed.

In all cases, single-phased, homogeneous in composition, nanostructured powders were obtained. Some of them exhibit excellent properties, such as medium-high range specific surface area, for potential application in catalysis and SOFC technology.

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1. Introduction

Among diverse wet-chemical methods for the synthesis of nanostructured materials, an excellent choice developed by years was the gel-combustion process (GCP): Stoichiometric and fuel-rich GCPs employing different fuels were intensively studied during almost last two decades. These GCPs are especially proper for the preparation of ceramic nanopowders, precursors for the fabrication of dense, ultrafine (nano and/or submicrometric) grained ceramic samples or pieces of pure or doped solid solutions of ZrO₂, CeO₂, and pure Al₂O₃. Composite samples of discrete, ultrafine grains of these oxides can be obtained as well.

This trend of scientific and technological research is widely recognised in pertinent literature, being its evolution evident (Lamas, 1998; Lascalea, 2004), mainly because these GCPs yield, in a conventional chemistry laboratory, a considerable amount (in the range of grams) of a compositionally homogeneous nanopowder of the metal oxide of interest. Even more, if necessary safe precautions and a prudential consideration of the resources were taken into account, these processes can be implemented to a greater scale that could yield 10-100 g or more per batch. GCPs are, then, versatile, low cost processes with an impressive experimental flexibility.

GCPs antecedents were the Pechini process (Zhang et al., 2002) and those experimental results reported in the somehow predictive letter from Chick et al., 1990, which established the base for our further research on GCP syntheses, early reported from our laboratories (Juárez et al., 2000). In a more recent, previous work (Lassa et al., 2009), the authors reported nitrates-EDTA and nitrates-TRIS GCPs as novel routes, and a set of preliminary results of the morphology and structure of the calcined nanopowders obtained via these processes.

After a steady research to complete an actual view about these particular routes, new, pertinent results of morphological and structural characterisation for calcined nanopowders of ZrO₂-CeO₂ obtained by fuel-rich or stoichiometric, nitrates-EDTA or nitrates-TRIS GCPs are reported in this work: all results were obtained/measured recently and represent a complementary set to those informed in the mentioned, previous work (Lassa et al., 2009).

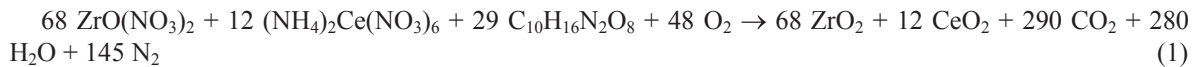
The characterization of obtained materials was performed by usual techniques as scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and some textural properties were evaluated employing our experimental Brunauer-Emmett-Teller (BET) isotherms.

2. Experimental procedure

2.1. Materials syntheses

Our fuel-rich GCPs start mixing appropriate proportions of the nitrates of the cations of interest and dissolving these precursors in aqueous solution, which is acidified with a slight excess of nitric acid. Then, the organic fuel (EDTA: ethylenediaminetetraacetic acid, or TRIS: tris(hydroxymethyl)aminomethane) is added and the solution is neutralized (pH = 7) with ammonium hydroxide diluted with distilled water. This precursor solution is concentrated on a hot plate at 350°C until gelling and subsequent combustion. The ignition is auto-sustained and propagates to all the gel. Finally, the resulting ashes are properly calcined in order to remove all the organic residues.

In case of stoichiometric nitrates-EDTA or nitrates-TRIS GCPs, these routes are simpler than fuel-rich ones: in an usual procedure, the metal precursors (nitrates) and the fuel are full dissolved in a reasonable excess of distilled water, this solution contained on a 1L beaker is put for a gradual evaporation over a hot plate at 300°C without external agitation, until gelification. When the obtained gel reaches a critical dryness, spontaneously ignites, and the combustion soon autolimitates and ceases. The remaining ashes, properly calcined, yield a mass of a nanopowder as the final, expected product. For stoichiometric GCPs the same precursors and reagents used in fuel-rich ones were employed, all of them were analytical grade, and their amounts were specified by the corresponding, proposed, stoichiometrically balanced process. As an example (1), it is detailed the proposed, stoichiometric reaction for the synthesis of the nanopowder of ZrO₂-15 mol% CeO₂, solid solution obtained by a nitrates-EDTA GCP:



The powders studied are identified as follows: X##Z, where X=R for stoichiometric processes, the omission of X indicates that the process is a fuel-rich GCP. Meanwhile, ## indicates the molar concentration (percentage) for cerium oxide (15 or 90) and Z is used to specify the chosen fuel (E for EDTA and T for TRIS). The time of calcination was two hours for all studied ZrO₂-CeO₂ powders, specified in Table 1.

Table 1. Powders of ZrO₂-CeO₂ studied.

GCP	Composition	Code
Stoichiometric nitrates-EDTA	ZrO ₂ -15mol%CeO ₂	R15E
Stoichiometric nitrates-TRIS	ZrO ₂ -15mol%CeO ₂	R15T: Process is not viable
Fuel-rich nitrates-EDTA	ZrO ₂ -15mol%CeO ₂	15E
Fuel-rich nitrates-TRIS	ZrO ₂ -15mol%CeO ₂	15T
Stoichiometric nitrates-EDTA	ZrO ₂ -90mol%CeO ₂	R90E
Stoichiometric nitrates-TRIS	ZrO ₂ -90mol%CeO ₂	R90T
Fuel-rich nitrates-EDTA	ZrO ₂ -90mol%CeO ₂	90E
Fuel-rich nitrates-TRIS	ZrO ₂ -90mol%CeO ₂	90T

2.2. Characterization of ZrO_2 - CeO_2 nanopowders

The crystalline phases of the resulting powders were studied by XRD by means of a Philips PW 3710 diffractometer, operated with $CuK\alpha$ radiation. The average crystallite size of these materials was evaluated from the broadening of the Bragg's peaks using the Scherrer equation (Klug and Alexander, 1974).

For agglomerate morphology observations by SEM two microscopes were employed: a Philips 505 or a brand new Jeol JSM 66LV, both operated with accelerating voltages ranging in 20-25kV and magnifications in the range of 500-5000x.

For higher magnifications, in bright field mode, a Jeol M2010 transmission electronic microscope was employed. For the preparation of specimens for TEM observations, thin agglomerate particles were fixed on the usual grill-type holders, previously coated with a film of cellulose acetate/butyrate formed via solvent evaporation of a solution of these organic compounds in ethyl acetate. In such film, holes formation was induced by addition of glycerin. The final step of this preparation is a coating with a carbon film to enhance the mechanical resistance of the specimen.

Textural properties (S_{BET} among others) were evaluated employing BET isothermes obtained by means of a Micromeritics Accusorb 2100 equipment.

3. Results and discussion

Fig. 1. a) and b) display selected XRD patterns as examples. These diffractograms demonstrate the retention of the metastable, tetragonal phase in nanopowders of ZrO_2 -rich composition (ZrO_2 -15mol% CeO_2) calcined at 600°C and of the cubic phase in the CeO_2 -rich (ZrO_2 -90mol% CeO_2) nanopowders calcined at same conditions. These results were similar for all nanopowders studied for this work and are in good agreement for the observed in the previous, preliminary studies (Lassa et al., 2009) in which, for certain selected cases, a calcination process at 350°C was performed. So, it was observed that tetragonal phase was retained, or cubic phase was obtained, as expected in each case, only taking into account the compositions, with independence of the calcination temperature in the range of 350-600°C.

As expected for powders prepared by these routes, it was observed their nanostructured nature in all cases, with average crystallite sizes similar to those reported in preliminary studies (Lassa et al., 2009) and not exceeding 40 nm in any case.

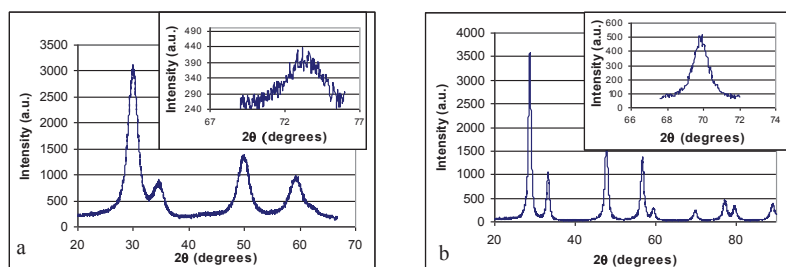


Fig. 1. X-ray diffraction patterns of: a) 15T. In the insert: high-angle peak (400)/(004), b) 90T. In the insert: high-angle peak (400)/(004).

By direct observation in bright field mode at very high magnifications (ranging 800,000-1,000,000x) by TEM, the nanometric size of the crystallites were properly checked: Fig. 2. a), b) and c) display, as examples, TEM micrographs of different, specified specimens.

In each of these micrographs, it can be clearly observed one discrete, submicrometric particle of agglomerate, built of visible and well defined nanocrystallites. An estimation of the size of these agglomerate particles was obtained by direct measure of their maximum lengths (ML) and an estimation of the corresponding average crystallite size (ACS) was made employing the intercept method, resulting for 15E specimen (Fig. 2. a) $ML(15E)=190\pm 1$ nm, $ACS(15E)=8\pm 1$ nm; for 15T specimen (Fig. 2. b) $ML(15T)=247\pm 1$ nm, $ACS(15T)=22\pm 1$ nm and for 90E specimen (Fig. 2. c) $ML(90E)=123\pm 1$ nm, $ACS(90E)=6\pm 1$ nm.

Fig. 3. a) and b), and 4. a) and b) are SEM micrographs of specimens obtained by nitrates-EDTA GCPs which are a new complement of observations reported in previous, preliminary results (Lassa et al., 2009). Fig. 3. a) is a micrograph of a 15E specimen observed at low magnification, in which are evident the typical agglomerates of different sizes, exhibiting a regular distribution of pores, meanwhile, in Fig. 3. b) the same specimen is observed at higher magnification, with a most detailed view of the porosity in such range of sizes.

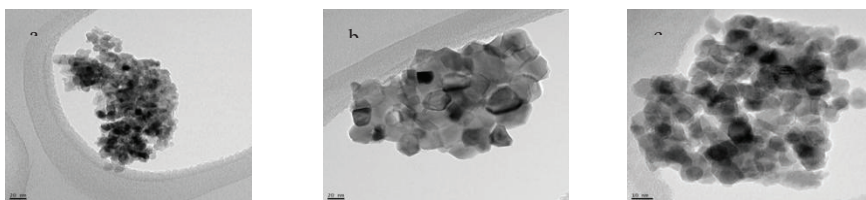


Fig. 2. TEM micrographs of: a) 15E specimen (bar = 20 nm), b) 15T specimen (bar = 10 nm), c) 90E specimen (bar = 20 nm).

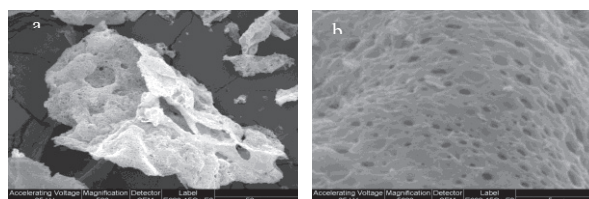


Fig. 3. SEM micrographs of a 15E specimen: a) Low magnification ($M = 500x$), b) High magnification ($M=5000x$).

Fig. 4. a) is a micrograph of a R15E specimen at low magnification, in which can be seen atypical (for GCPs), mainly non porous agglomerates obtained by a stoichiometric process. Fig. 4. b), in turn, is a micrograph of the same specimen observed at higher magnification, in which it can be clearly seen the regularity of the agglomerate particle and the particular structure of the pores. These observations correlate well with the S_{BET} value obtained for that nanopowder.

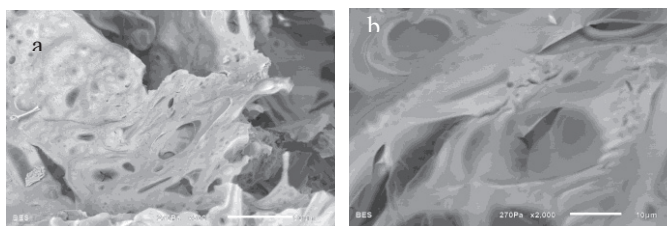


Fig. 4. SEM micrograph of a R15E specimen: a) Low magnification ($M = 500x$), b) High magnification ($M = 2000x$).

In Table 2, textural properties of various, obtained powders are reported, including at least one from a stoichiometric GCP. Values of specific surface areas reported are of mid-high range regarding the case. The corresponding, average crystallite size evaluated using the Scherrer's equation were also included.

Table 2. Textural properties results from various obtained powders.

Specimen	Average crystallite size (nm)	Specific surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (Å)
15T	20±1	40±4	0,154±0,002	130±10
15E	7±1	36±4	0,060±0,001	73±7
R15E	6±1	29±3	0,047±0,001	65±7
90T	30±1	101±10	0,289±0,004	120±10
90E	5±1	27±3	0,054±0,001	80±8

4. Conclusion

Both stoichiometric and fuel-rich GCPs studied, yield nanostructured, single-phased powders with the expected crystalline phase retained/obtained in each case. Some of these powders exhibit excellent properties for potential applications in the catalysis area or for SOFCs anodes development.

It must be especially mentioned that, in all case of preparation of CeO₂-rich powders (ZrO₂-90 mol%CeO₂) it was observed a less violent reaction compared with the (almost not viable) nitrates-glycine GCPs allowing the recovery of all ashes formed, which lead to reach acceptable yields. This allows, in turn, to have enough mass of these powders for further ceramic studies like well sintering for dense specimens fabrication of these compositions. In the case of nitrates-TRIS GCP CeO₂ rich powders, a remarkable high specific surface area is observed.

Notwithstanding stoichiometric GCPs are more simple processes, both regarding their instrumentation or their conceptual consideration, in the frame of our observations for this study, they seem not to allow to prepare powders with high specific surface area, which correlate, additionally, with the low poral volume measured. The morphology of these powders neither seems to be promising for the use of them both for preparation of thick films or dense ceramics since the powders do not seem to be "reactive" enough, as the fuel-rich GCPs derived powders are for sure [Lascalea 2004, Juárez et al. 2000].

It was observed, in addition, that some proposed, stoichiometric GCPs were not viable because of an early and irreversible precipitation at the precursor solution stage, which, in turn, inhibit to reach the gel formation stage, cancelling all possible GCP preparation in these cases: in a general frame, when a stoichiometric condition is established, the course of the whole process result very restricted and, in some cases, it is chemically incompatible causing their non-viability.

With the above mentioned observations taken into account, at least for ZrO₂-CeO₂ powders, it could be affirmed that stoichiometric nitrate-EDTA or nitrates-TRIS GCPs does not prove to provide better results than the fuel-rich ones. Then, it is proposed here that, in future experimental works, focus must be put on fuel-rich GCPs employing, as valid alternatives for research, some more economic and affordable fuels as carbohydrates.

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