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Synthesis and Characterization of Doped Cerium Nanocatalysts Samples Through Nitrate Solutions Thermal Decomposition

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Abstract**—** *Ceria based catalysts doped with calcium, zinc, magnesium were synthesized to the future application in the fast pyrolysis biomass in order to improve the kinetics towards volatile hidrocarbons production. Through thermal treatment of nitrate aqueous solutions followed by calcination of the produced solid powder at 600ºC, solid solutions of CeO_2 doped with Ca, Zn and Mg have been successfully synthesized. The final solid samples have been characterized through X ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS), in order to evaluate both the elemental composition, as well as the nature and amount of each crystalline phase (Rietveld analysis). The results show that in all cases the desired solid solutions have been obtained, with a mean crystallite size lying in the range between 9.5nm to 34.9nm, suggesting the presence of nanostructured particles.*

Keywords**— CeO_2, Nitrate, Thermal Decomposition.**

I. INTRODUCTION

Catalysts applicability is rising, especially in chemical and petrochemical industries. The search for an ideal catalyst is incessant, especially in relation to factors that lead to deactivation or poisoning because nowadays the focus for a process is to have a good optimization and get high performance and stability. [1].

In heterogeneous catalysis, the surface area should be as higher as possible, in order to maximize the exposition of the catalyst surface to the reactive media, which maybe achieved with nanostructured catalysts. Oliveira et al. [2] and Ramos et al. [3], emphasized that thermal decomposition through nitrate solutions is a viable method for producing nanoparticle materials because they are attractive and generate a completely homogeneous dispersion of the second phases in the metal matrix. Thus, they can obtain superior surface area, proving to be a very promising method because it involves low temperatures and short synthesis time. According to the current literature, metal oxides are promising materials for use as nanocatalysts, as the acid and base sites can be optimized by inserting specific dopants and also due to the possibility of producing nanostructures by different synthesis approaches, such as butadiene and biodiesel production, which use heterogeneous catalysis to obtain quality and selectivity of materials [4,5].

In this context, ceria oxide (CeO_2) has gained considerable attention from scientific community, especially through its application as a three-way catalyst, thereby stimulating the conversion of oxidized pollutant molecules, such as CO and NOx to CO_2 and N_2, the high selectivity and conversion achieved, a consequence of significant oxygen mobility in the cubic crystalline structure [6]. Moreover, when used as a support for metallic particles, the resulting strong interaction contributes for the high selectivity observed [7].

Marinković et al. [8] verified that catalysts containing calcium oxide and magnesium oxide are promising materials to be used as heterogeneous catalysts in biodiesel production due to high efficiency in transesterification reaction. According to Borges and Díaz [9], CaO presents interesting properties for this kind of reaction such as high activity, long catalyst life and requires moderate reaction conditions. Ferreira [10] studied the pyrolysis process using two types of raw materials, sugarcane biomass and Macaúba pulp presscake. The obtained results indicated that CaO increased non-condensable gases levels supporting the idea that the catalyst application in the gasification process of biomass should increase in a near future, due to low cost and its favoring in relation to the synthesis gas with lower CO_2 formation, a possible byproduct of this process. In this context, Nokkosmäki

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[11] has shown that ZnO, a recognized basic oxide, can also function as an excellent catalyst for bio-oil formation through rapid pyrolysis of pine sawdust, improving the chemical stability of the treated oil and significantly increasing the viscosity of the oil. around 55%.

In the present work cerium oxide samples doped with calcium, zinc or magnesium were synthesized through co-precipitation from thermal treatment of aqueous nitrate solutions. Next, the synthesized materials were characterized by scanning electron microscopy and energy-dispersive spectroscopy (SEM/EDS) and X ray diffraction (XRD), in order to evaluate both the elemental chemical composition, and also to quantify the crystalline phases present, confirming the production of the ceria solid solutions of interest.

II. METHODOLOGY

2.1. Surface Mixed Oxide Synthesis

The synthesis procedure starts with preparation of 0.05 M aqueous solutions of analytical grade zinc ($Zn(NO_3)_2.6H_2O$), calcium ($Ca(NO_3)_2.4H_2O$) and magnesium ($Mg(NO_3)_2.6H_2O$) powders. Next, 75mL of each dopant solution was mixed with the same volume of a 0.1624 M aqueous cerium ($Ce(NO_3)_3.6H_2O$, PA) nitrate solution.

The final solution was then thermal treated in a blanket for 120 minutes reaching around 250°C and the resulting powders calcined at 600°C for 3 hours in muffle furnace, open to the atmosphere. Table 1 presents the dopant included in each sample, together with specific labels for future reference in the discussion of the results.

Table 1. Synthesized samples.

A. Sample	B. Dopant metal
C.	D.
E. A	**F.** Ca^{+2}
G. B	**H.** Mg^{+2}
I. C	**J.** Zn^{+2}

2.2. Characterization

After synthesis, each catalyst sample has been characterized through SEM/EDS, in order to evaluate both surface morphology and elemental chemical composition. For accomplish this analysis, a HITASHI tabletop microscope was employed, model TM 3000, which works with back scattered electrons and 15kV accelerating voltage.

For the identification/quantification of the crystalline phases formed, XRD analysis has been performed through use of a Bruker diffractometer, model Discover 8, which works with Cu source and is equipped with a high precision lynxeye detector. The XRD data was next analyzed through Rietveld method with fundamental parameters, which has been applied through use of software TOPAS 5.0 (Bruker). This analysis was especially important for the research, in order to confirm that the doping process has been successful, as well as for the evaluation of the sample mean crystallite size, a parameter directly related to the nanostructured content.

III. RESULTS AND DISCUSSION

On Figure 1 the XRD data for sample A can be seen. The Rietveld modelling has been performed with a CIF type file based on the structure published by Mohanty et al. [12], which consider a CeO_2 cubic solid solution, whereas the atomic fractions of Ce^{+4} and Ca^{+2} are respectively equal to 95 and 5%, and where kept constant during the refinement.

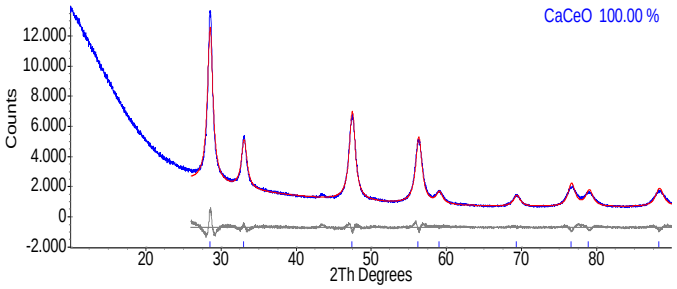

Fig.1: XRD data after Rietveld analysis from sample A.

The results point out the presence of a single crystalline phase of the mentioned solid solution, whose large diffraction peaks should be associated with the presence of nanostructured crystals. The quality of the Rietveld refinement can be attested as of quantitative level, indicated by the gray bottom line, which depicts the difference between experimental and calculated diffraction intensities.

On Figures 2 and 3, the results from SEM/EDS analysis performed on sample A can be observed. The gray scale contrast suggests the presence of a monophasic material in accordance to the information obtained by the Rietveld analysis (Figure 1).

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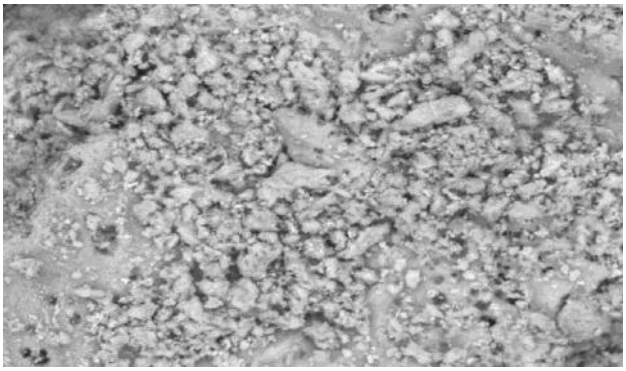
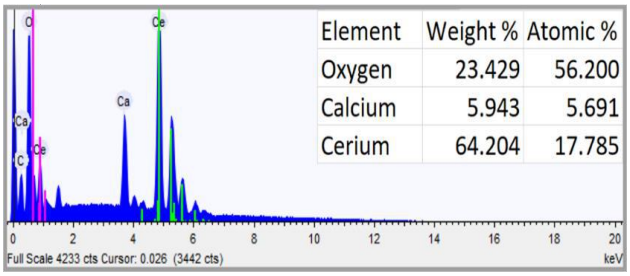


Fig.2: SEM micrograph of catalyst sample A (magnified 2000X).

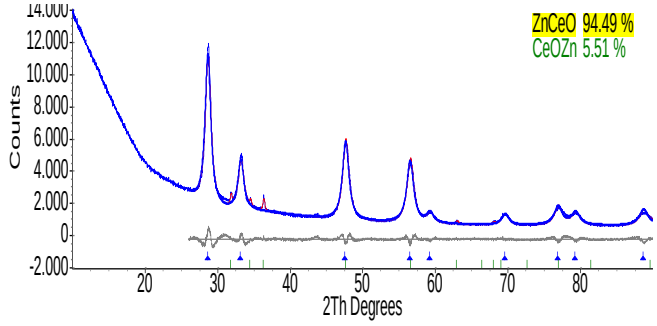
As expected, the chemical composition determined through EDS (Figure 3), indicates the presence of Ce, O and Ca atoms, Ce and O being the atomic entities of much higher concentration, both explained by the fact that CeO_2 plays the role of a solvent, and CaO the solute. The peak not labeled, localized around 1,5 kev, and which is present in the EDS signals of all other samples, should be associated to aluminum, an element contained in the sample holder.



Element	Weight %	Atomic %
Oxygen	23.429	56.200
Calcium	5.943	5.691
Cerium	64.204	17.785

Fig.3: EDS signal and elemental composition of catalyst sample A.

On Figure 4 the result from Rietveld refinement of XRD data of sample B can be observed, which was achieved based on CIF files constructed from data of Wook [13] and Torres-Huerta [14].



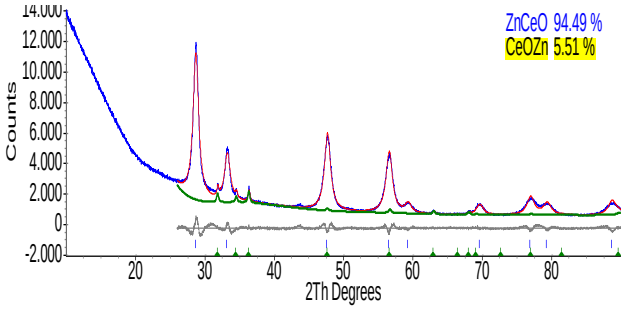


Fig.4: XRD data after Rietveld analysis from sample B.

As in case of sample A, the presence of large peaks suggests a significant nanostructured content. The assessment quality is evident from the very low difference between experimental and calculated intensities. According to Figure 4 is realized that this sample has two different solid phases. In the cubic structure, CeO_2, majority element, was doped with 3% of zinc, dopant element. For the other one, cerium as dopant element was incorporated into the zinc structure. The main explanation for this existence is that the solubility limit of zinc in the ceria structure could be reached.

The micrograph obtained through SEM of sample B is presented on Figure 5. A careful look at the micrograph shows that the gray scale contrast is not uniform, suggesting that the distribution of Zn and Ce should not be uniform, which could be explained by the hypothesis that two phases are present, as confirmed through XRD analysis (Figure 4).

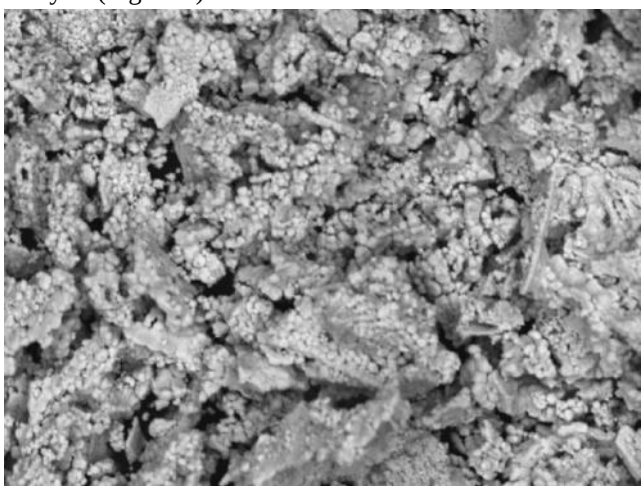


Fig.5: SEM micrograph of catalyst sample B (magnified 2000X).

The EDS spectrum of the area depicted on Figure 5 is in accordance to the expectations, the mass fraction of Zn, the dopant, much lower than the one for Ce.

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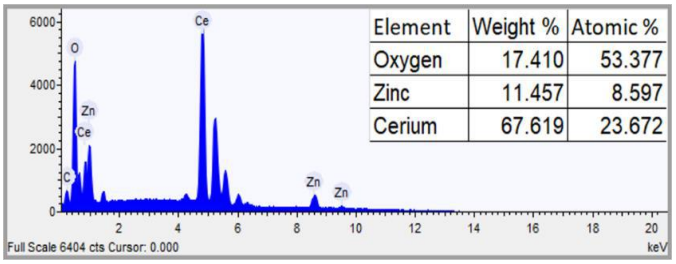

Fig.6: EDS signal and elemental composition of catalyst sample B.

Figure 7 depicts the refinement of sample C XRD data. The Rietveld method was executed with a CIF file based MgO structure published by Boiocchi [15].

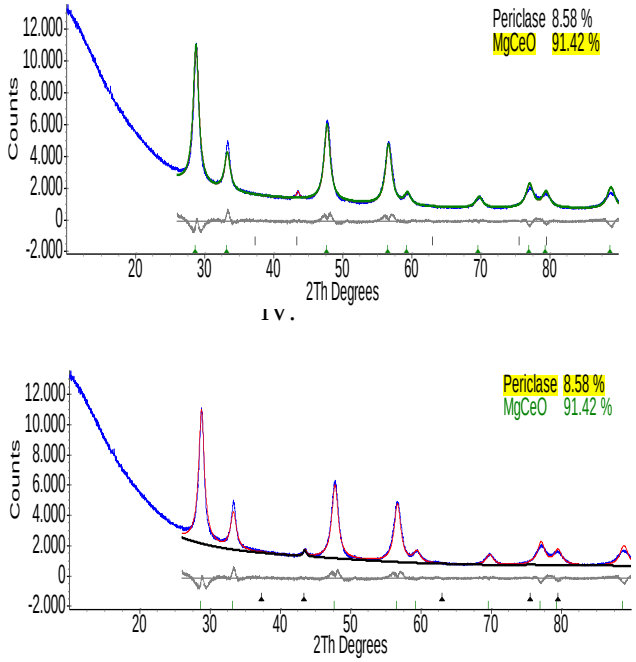

Fig.7: XRD data after Rietveld analysis from sample C.

The quality of the adjustments could be seen as a quantitative analysis due to model curve is sufficient close to the experimental values. The results show that there was obtained a nanostructured material confirmed by the extended peaks of the figure 7. The peak showed in 44 (2Th Degrees) refers to the MgO structure, indicating a small percentage of this structure in this sample, which suggest that the solubility limit of Mg was achieved.

Figure 8 presents a micrograph of sample C, and as in the case of sample B (Figure 6), some variations in the gray scale intensity can be also be detected, suggesting that the material should contain at least two phases, as confirmed through XRD analysis (Figure 7).

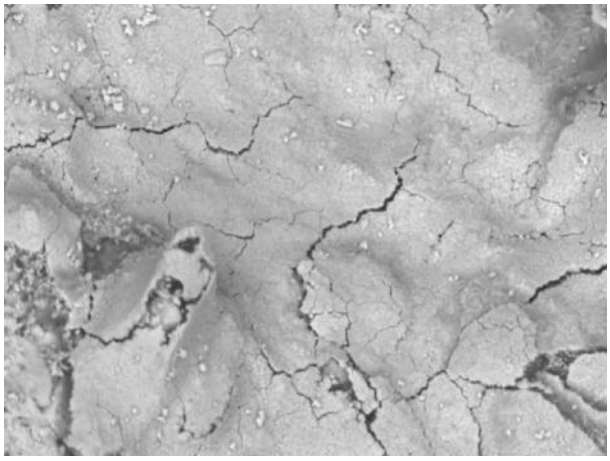

Fig.8: SEM micrograph of catalyst sample C (magnified 2000X).

On Figure 9, EDS data for sample C is presented. As in case of all other samples, Ce is the major element, followed by oxygen and the dopant, Mg in the present case. Besides the peak of aluminum (1,5 keV), no signals from impurities are observed.

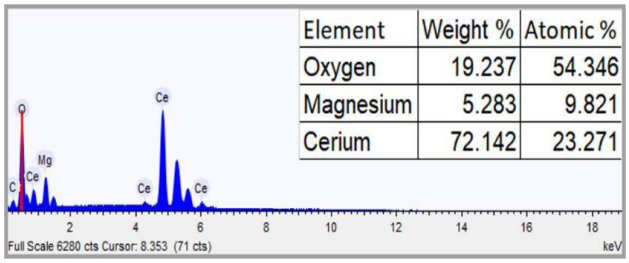

Fig.9: EDS signal and elemental composition of catalyst sample C.

As said before, the significant spreading of the diffraction peaks suggests the presence of crystalline regions with sizes in the nanometric range. Indeed, the determined crystallite average sizes during Rietveld analysis confirms this tendency (Table 2).

Table 2. Crystallite average size regarding each synthetized sample.

Sample	Crystallite average size (nm)
A	CaMgO - 10.8
B	ZnCeO - 9.5 ; CeOZn- 34.9
C	MgO- 20.2 ; MgCeO- 9.5

V. CONCLUSION

The synthesis of doped nanocatalysts based on ceria was shown to be effective by the thermal decomposition method, especially for the samples with Ca and Mg.

Through the XRD analysis and the quality of the graph adjustments in the quantitative levels by the Rietveld method, it can be concluded that the formation of nanostructured materials occurred, thus considering the successful reagent doping due to the extended peaks and their size. average crystallite between 9.5 nm and 34.9 nm.

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However, it can be noted that one of the cases occurred excess solubility. Mostly, the solids solutions of interest (CaO/CeO_2, ZnO/CeO_2, MgO/CeO_2) were formed. Due to the excess of MgO, and thus, its lack of solubility others crystalline phases were identified in samples B and C, being in the first sample a non-cubic structure with cerium incorporating on the structure of ZnO and in the second, in the presence of a small percentage of MgO on the structure of the material.

The results obtained by SEM confirm the monophasic nature of samples A and C due to the lack of color contrast in the micrographs, however, the data suggest that sample C presents more than one phase in the XDR. In the case of sample B, the gray contrasts present in the analysis confirm the synthesis of a biphasic material. The EDS spectra corroborate the expected elemental composition for each sample, indicating the absence of impurities, and the greater presence of Ce.

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REFERENCES

[1] Schmal M. Catálise Heterogênea. Rio de Janeiro: Synergia; 2011.

[2] Oliveira M J C, Quirino M R, Neiva L S, Gama L, Oliveira J B. Síntese de óxido de cério (CeO_2) com alta área superficial por meio do método hidrotérmico assistido por micro-ondas. Revista Eletrônica de Materiais e Processos. v.6.3, p. 170-174, 2011.

[3] Ramos, M. I., et al. "Microstructure Investigation of Cu-Ni Base Al2O3 Nanocomposites: From Nanoparticles Synthesis to Consolidation." *Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science*, vol. 48, no. 5, Springer US, 2017, pp. 2643–53, doi:10.1007/s11661-017-4000-6.

[4] Chagas, L. H.; Matheus, C. R.V.; Zonetti, P. C.; Appel, L. G. Butadiene from ethanol employing doped t-ZrO2. *Molecular Catalysis*. vol.458, p. 272-279, 2018.

[5] Fernandes, R.; Oliveira C. R.; Martins M. I.; Cardoso V. L. E Reis M. H. M. PRODUÇÃO DE BIODIESEL POR CATÁLISE HETEROGÊNEA USANDO ÓXIDO MISTO CaO-CeO2 COMO CATALISADOR. XI Congresso Brasileiro de Engenharia Química em Iniciação Científica, XI COBEQ-IC. Unicamp, SP, 2015.

[6] Martins Tereza S, Hewer Thiago L R, Freire Renato S. Cério: Propriedades catalíticas, aplicações tecnológicas e ambientais. Química Nova. 2007; 30 (8): 2001-2006.

[7] Sun C, Li H, Chen L. Nanostructured ceria-based materials: synthesis, properties, and applications. Energy & Environmental Science. 2012; 5: 8475-8505.

[8] Marinković D M, Stanković M V, Veličković A V, Avramović J M, Miladinović M R, Stamenković O O et al. Calcium oxide as a promising heterogeneous catalyst for biodiesel production: Current state and perspectives. Renewable and Sustainable Energy Reviews. 2016; 56: 1387–1408.

[9] Borges M E, Díaz L. Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: A review. Renewable and Sustainable Energy Reviews. 2012; 16: 2839-2849.

[10] Ferreira, Nathália de Lima. Pirólise de biomassa lignocelulósica utilizando diferentes catalisadores para a produção de bio-óleo. Belo Horizonte: Universidade Federal de Minas Gerais; 2014.

[11] Nokkosma M I, Kuoppala E T, Leppa E A. Catalytic conversion of biomass pyrolysis vapours with zinc oxide. Journal of Analytical and Applied Pyrolysis. 2000; 55: 119-131.

[12] Mohanty B C, Lee J W, Yeon D H, JO Y Hwa, KIM Jong Hak, CHO Y S. Dopant induced variations in microstructure and optical properties of Ce O2 nanoparticles. Materials Research Bulletin. 2011; 46 (6): 875-883.

[13] Wook L S, Dojin K, Huijun W, Wonyang C. Electrical conductivity and defect structure of (Ce O2)-(Zn O) system. Electronic Materials Letters (2006) 2, (1) p. 53-58.

[14] Torres-Huerta A M, Domínguez-Crespo M A, Brachetti-Sibaja S B, Dorantes-Rosales H, Hernández-Pérez M A, Lois-Correa J A. Journal of Solid State Chemistry Preparation of ZnO : CeO 2 – x thin films by AP-MOCVD : Structural and optical properties. v.183, p. 2205-2217, 2010.

[15] Boiocchi M, Caucia F, Merli M, Prella D, Ungaretti L.Crystal-chemical reasons for the immiscibility of periclase and wüstite under lithospheric P, T conditions, European Journal of Mineralogy. 2001; 13: 871-881.