

## APPLICATION OF CERIUM OXIDE FIBERS OBTAINED BY ELECTROSPINNING IN THE CATALYTIC COMBUSTION OF METHANE

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### ABSTRACT

*In this work cerium oxide fibers, doped with copper, were synthesized using the electrospinning process. Cerium acetylacetonate was used as a precursor in the electrospinning synthesis. The obtained fibers were heat treated at 650°C. The non-tissue material obtained was characterized by X-ray diffraction to determine the phase and crystallite size, BET method to determine the surface and SEM to analyze the microstructure of the fibers. The catalytic activity was evaluated by methane and air combustion under different temperatures. The amount of combustion gases such as NO<sub>x</sub>, C<sub>x</sub>H<sub>y</sub>, CO e CO<sub>2</sub>, were analyzed.*

**Topic 4:** Ceramic Materials

**Key words:** catalysis, cerium oxide, electrospinning.

### 1. INTRODUCTION

Interest in the study and applications of nanoparticles has been growing in recent years, mainly because of its unique physical and chemical properties, that make them significantly different from its usual microstructure [1]. Nanostructure particles exhibit a better sinterability, and a high catalytic activity due to high superficial area and surface properties [2].

The technique of electrospinning has been recognized as a versatile and effective method of producing fibers with very small diameters and high surface-volume ratio [3]. The morphology and properties of fibers depend on the characteristics of the polymer and the process parameters used, for example, average molecular weight of polymer, solvent, viscosity and conductivity of solution, electric field strength applied and collector distance [4,5,6].

The use of three-way catalysts is an accepted current method for controlling the emission of polluting gases. These catalysts are generally formed by the support, stabilizers, precious metal and transition metals, being the most widely used metals of the platinum group [7].

The use of cerium as a promoter is normally related to its ability to store oxygen [8] and structural aspects such as the property of increasing the dispersion of metals and to change slowly the support phase stabilizing it.

On the other hand, copper has been explored as a possible replacement for palladium and platinum in the reduction of NO by CO [9]. Despite the importance of oxidation of CO on Cu, the reaction is not elucidated because changes in the oxidation state when the reaction conditions are changed. Somorjai and coworkers [10] studied the catalytic activity of Cu<sup>0</sup>, Cu<sup>+</sup> and Cu<sup>2+</sup>. The results indicated that the catalytic activity for CO oxidation decreased from Cu metal to Cu<sup>2+</sup> and was inhibited by oxygen. The type of mechanism was explained by Langmuir-Hinshelwood where adsorbed CO reacts with adsorbed oxygen. To take place the reaction the oxygen should be decoupled. For Cu<sup>+</sup>, the higher activation energy found in relation to Cu<sup>0</sup> was explained as extra energy for the dissociation of O<sub>2</sub>.

In this paper, fibers of cerium oxide doped or not with copper were obtained from a solution of cerium acetylacetonate, copper nitrate and polyvinylpyrrolidone (PVP). After heat treatment, fibers of cerium oxide were obtained. These fibers were structurally characterized by scanning electron microscopy (SEM) had its specific surface area determined by BET, were subjected to thermogravimetric test to monitor their thermal decomposition were analyzed by X-ray diffraction to determine the phase present. The catalytic activity was evaluated by monitoring the amount of O<sub>2</sub> consumed and CO and CO<sub>2</sub> formed, for the combustion of methane and air.

## 2. EXPERIMENTAL

### Materials

A precursor was made by mixing of 2.15g of cerium acetylacetonate (Aldrich), 2mL of anhydrous ethanol and 21mL 10% alcoholic solution of polyvinylpyrrolidone (PVP). To evaluate the effect of the presence of copper in the catalytic activity of the fibers, sufficient amount of copper nitrate was added to the solution to provide 0.5, 1.0 and 2.5 mol% copper.

To measure the catalytic activity of this material was used a muffle furnace with a quartz tube mounted vertically inside. Inside this tube was added the catalyst (0.20g) in presence of flow of methane (99.995% purity) of 0.1 L/min synthetic air (20% O<sub>2</sub> and 80% N<sub>2</sub>) of 0.9 L/min. The amount of gases C<sub>x</sub>H<sub>y</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, NO, NO<sub>x</sub> was measured using a portable gas analyzer Euroton model Ecoline 4000.

### Electrospinning

From the mixture of cerium acetylacetonate, copper acetate and PVP fibers were obtained using the technique of electrospinning.

On a typical electrospinning process, the solution precursor is loaded into a 5mL syringe attached to a hypodermic needle 12-Gauge. The needle is connected to a high voltage supply. The strain used for fiber formation was about 10 a 13 kV, applied at a distance of 12 cm of a counterelectrode cylindrical, which was covered with an aluminum foil. The fluid flow was controlled by an infusion pump, and kept constant at 0.8 mL/h.

### Characterization

The crystalline phases present were identified through analyses by X-ray diffraction using a Philips equipment (model X'Pert MPD) and operation at 40 kV and 40 mA, with CuK $\alpha$ . The analysis was performed at a rate of 0.05°/min, with a step of 1 sec in the range of 5 to 75°.

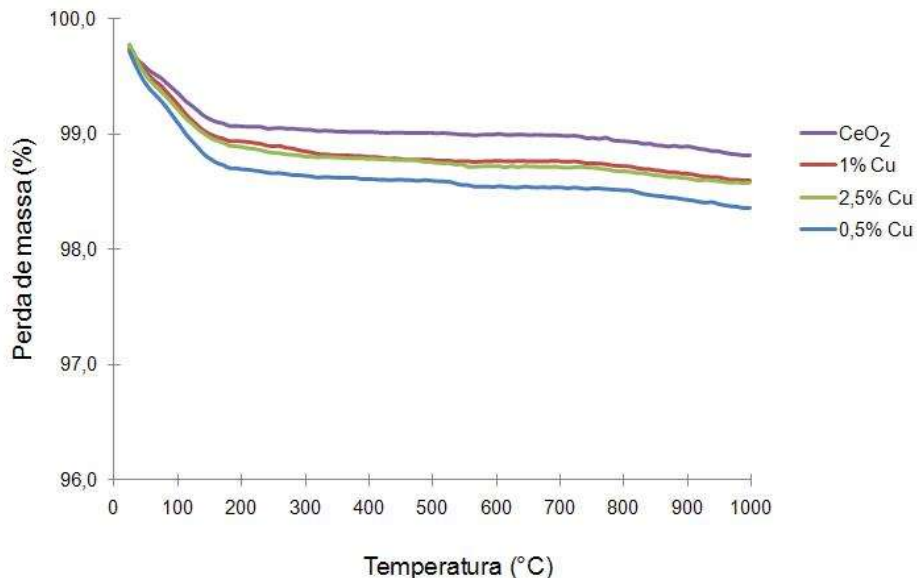
The morphology of the powder produced in this work was observed by scanning electron microscopy (SEM) using a Jeol equipment (model JSM 5800). A thin gold layer was deposited on the sample surface to make it conductive.

Thermogravimetric analysis (Metler & Toledo SDTA 851 TGA) was performed at 1000°C with a heating rate of 10°C/min in synthetic air atmosphere.

The specific surface area (Nova 1000 QuantaChrome) was determined by BET (Brunauer-Emmett-Teller) using N<sub>2</sub> as a gas adsorbent. The samples were previously prepared in vacuum at 200 °C for 2 hours.

### 3. RESULTS AND DISCUSSION

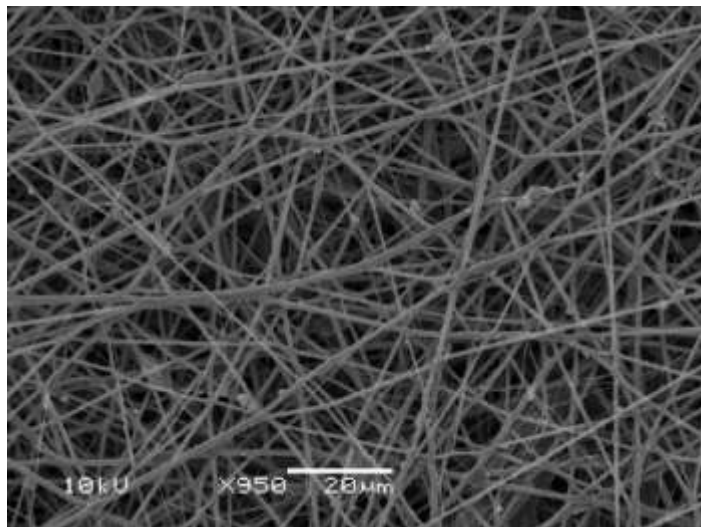
The thermal decomposition of the cerium, copper, PVP, composite fibers after heat treatment was followed using thermogravimetry, as depicted in Figure 1.



**Figure 1.** Thermal analysis of the fibers containing cerium, copper and PVP, after heat treatment.

The thermogravimetric analysis curve shows a continuous mass loss of the sample to about 150° C. This loss, approximately 1.5% is probably caused by loss of water present in the fiber structure. Above this temperature there are no other significant losses of mass. Thus, we find that the heat treatment performed at 650°C was sufficient to remove all organic compounds and volatile (PVP, alcohol and nitrates) in the fiber after its synthesis.

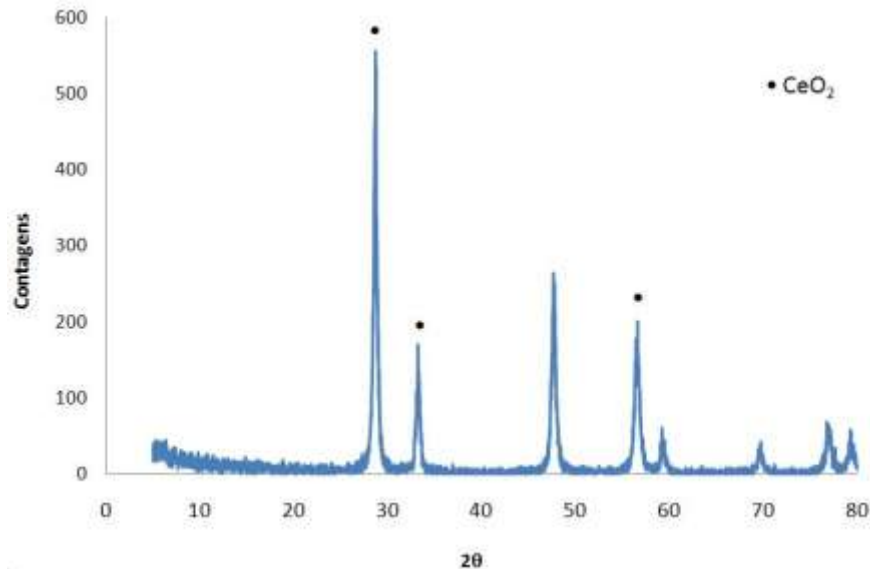
The fiber morphology was examined using the scanning electron microscope (SEM). Figure 2 shows the SEM image obtained after heat treatment at 650 ° C.



**Figure 2.** SEM of fibers obtained by electrospinning after heat treatment 650°C.

The average fiber diameter is 100nm after thermal treatment. If we compare the diameters before and after heat treatment there is a reduction of the diameter of the fibers caused mainly by loss of organic compounds during heat treatment. The specific surface area (SSA) determined by BET of the cerium oxide fibers containing 1% copper, annealed 650°C was 55.56 m<sup>2</sup> / g.

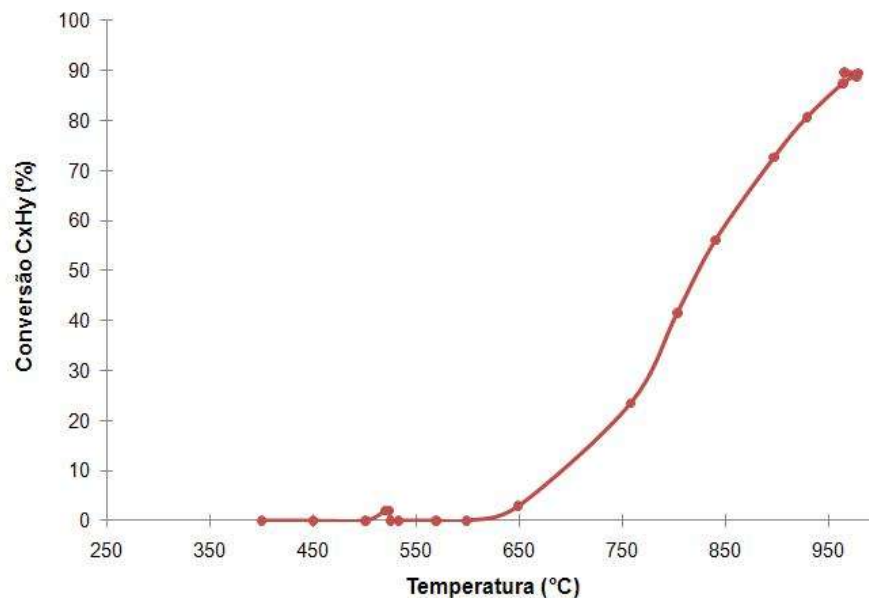
Figure 3 presents the analysis of X-ray diffraction (XRD) of the fibers after heat treatment performed at 650°C. In all formulations, regardless of copper content, we can observe only the presence of cerium oxide phase. The presence of phases containing copper was not detected due to limitations of the technique of X-ray diffraction



**Figure 3.** X-ray diffractogram obtained by electrospinning fibers after heat treatment 650°C.

The catalytic activity of the fibers was measured by analyzing the gases consumed and generated during heating to 600°C in a mixture containing 10% methane and 90% synthetic air with flow rates of 900mL/min of synthetic air and 100ml / min of methane. First trials were carried out without catalyst, only heating the gas mixture. The quantities of gases C<sub>x</sub>H<sub>y</sub>, O<sub>2</sub>, CO<sub>2</sub>, remained constant. The formation of CO, NO or NO<sub>x</sub> during the heating of gases in the absence of the catalyst was not detected. Figure 4 represents a diagram of the test catalytic combustion in the presence of CeO<sub>2</sub> catalyst containing 0.5% copper. The figure shows the degree of methane conversion during the reaction at different temperatures. In the presence of about 0.20 g fiber synthesized by electrospinning, containing cerium oxide and 0.5% copper, the beginning of the combustion process was about 525°C, when we begin to observe a jump in temperature of the reaction, a decreased in the amount of C<sub>x</sub>H<sub>y</sub> and O<sub>2</sub> and an increase in the amounts of CO<sub>2</sub>, CO, NO and NO<sub>x</sub>

Varying the concentrations of copper observed in general a decrease in ignition temperature, indicating a higher activity of the catalyst for the reaction with methane. In the sample without copper the beginning of the reaction temperature was 550°C. Samples containing 0.5, 1.0 and 2.5% copper, the beginning of the reaction occurred at 525, 500 and 560°C, respectively.



**Figure 4.** Methane conversion during the catalytic combustion, catalyst CeO<sub>2</sub>-0, 5% copper.

#### 4. CONCLUSIONS

Fibers of cerium oxide and copper were obtained by electrospinning technique. SEM images show fibers oriented randomly in the substrate. TEM images show that the fiber diameter is about 100nm and the size of its crystallites of about 17nm.

The catalytic activity of the fibers was significant. In the absence of catalysts until the temperature of 600°C there was a combustion reaction of methane and air mixture to the flow of gases used. In the presence of catalyst, the combustion reaction started around 550 ° C, with the consumption of methane and oxygen and the formation of CO and CO<sub>2</sub>. The formation of NO and NO<sub>x</sub> in the presence of the catalyst was not notice.

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