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Characterization and thermal behavior of $PrMO_3$ (M = Co or Ni) ceramic materials obtained from gelatin

F.M. Aquino [a,*], D.M.A. Melo [a], P.M. Pimentel [b], R.M. Braga [a], M.A.F. Melo [a], A.E. Martinelli [a], A.F. Costa [a]

[a] Federal University of Rio Grande of Norte, Laboratory of Catalysis and Refining – NUPRAR, Av. Senador Salgado Filho, 3000, CEP 59078-970, Natal-RN, Brazil
[b] Universidade Federal Rural do Semi-Árido, Campus Angicos, CEP 59515-000, Angicos-RN, Brazil

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ABSTRACT

Metal oxides with perovskite-type structure have attracted considerable interest in recent years due to their magnetic and electrical properties, as well as their catalytic activity. In this study, oxides with $PrNiO_3$ and $PrCoO_3$ composition were prepared by using gelatin powder as a precursor agent for its use as a catalyst. The powders obtained were calcined at 700 °C and 900 °C and characterized using the X-ray diffraction, thermal analysis (thermogravimetry and differential thermal analysis), infrared spectroscopy, temperature programed reduction and scanning electron microscopy techniques. Thermogravimetric data using the non-isothermal kinetic models of Flynn and Wall and "Model-free Kinetics" were used to determine the activation energy to study the decomposition kinetics of the ligand groups with system's metallic ions that takes part in the synthesis of $PrMO_3$ (M = Ni or Co).

1. Introduction

Rare earth cobalt and nickel oxides, $PrMO_3$ (M = Co or Ni), have been extensively studied due to their interesting electrical and magnetic properties. The $PrMO_3$ family, in particular Co or Ni, provides an interesting window for studying the evolution of the electronic characteristics of the oxides that display metallic conductivity [1–3].

In general, these properties are potentially influenced by the synthesis method, the calcination conditions (temperature, time, and atmosphere) and substitutions of the A and/or B sites. There are several methods for obtaining ceramic oxides with perovskite-type structures. Recent studies make use of gelatin as a polymerization agent and this process appears as a new alternative for obtaining materials with high efficiency and low cost [4].

A preliminary thermogravimetric analysis is sufficient for verifying the temperature at which these oxides are stabilized and the thermal behavior of the material studied. Thermogravimetric analysis (TGA) is one of the most commonly used technologies to study a variety of primary reactions of decomposition of solids and estimate the kinetics parameters of these processes [5].

Thus, a study was conducted on the thermal degradation of organic matter, derived from the gelatin used as a organic precursor in the synthesis of $PrNiO_3$ and $PrCoO_3$ powders, which is connected to metal ions in the system, using the kinetic models of Flynn and Wall and "Model free Kinetics", in order to establish the apparent activation energy as a parameter to characterize and optimize the synthesis conditions for the applicability of the material.

One goal of this work was to synthesize compounds without using high oxygen pressure and long time of calcination. One of the advantages of this method was produce powders with large amount of porous, with the future goal of their application in catalysis. The method is also a quick and easy route which use low-cost precursor, the gelatin. The disadvantages is the appearance of other phases, but probably disappear if we had increased the calcination time, which would not be interesting, since such materials would be further tested as catalysts and the long time of calcination result in a material with lesser superficial area and fewer porous.

2. Experimental

2.1. Synthesis of oxide powders

A modified Pechini method was used to synthesize the $PrNiO_3$ and $PrCoO_3$. Perovskites were synthesized by using gelatin as a precursor organic and metallic nitrates as starting reagent [5]. Initially, nickel nitrate or cobalt nitrate (Aldrich Chem, 99.9%) was added to a beaker containing deionized water under constant stirring between 60 °C and 70 °C for 5 min. Praseodymium (III) nitrate hexahydrate was added and the system was homogenized for another 5 min. Gelatin was then added to the solution at 70 °C

* Corresponding author. Tel.: +55 84 3211 9241.
E-mail address: flavyma@hotmail.com (F.M. Aquino).

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and stirred for 40 min. Next, the temperature was increased to 90 °C for 1 h, resulting in a resin. After being heat-treated at 350 °C for 2 h, the primary composite oxides were calcined at 700 °C and 900 °C for 4 h.

2.2. Materials characterization

The obtained ceramic powders were characterized by various techniques. Infrared absorption spectroscopy (IR) was carried out using KBr pellets. A Shimadzu IR Prestige-21 instrument was used to scan the range of 4500–400 cm^{-1}. X-ray diffraction was performed using Cu Kα radiation (λ = 0.15418 Å) in a Shimadzu XRD-6000, the diffraction angles (2θ) were scanned in a range varying between 10° and 90° with a step 0.02° and identification of the compounds were performed by comparison with data from JCPDS – International Center of Diffraction Data. Temperature programed reduction (TPR) was performed in Micromeritics AUTOCHEM II equipment. The powder with an average weight of 20 mg was heated at a rate of 50 mL min^{-1}, temperature 30° to 1000 °C, under a gas flow of 10% H_2/Ar. The scanning electron microscopy images were obtained using Philips XL – 30 ESEM equipment, with a power supply of 20 kV. The thermal analysis (TG and DTA) used for the experiments were carried out simultaneously using Shimadzu 60H equipment. Because the Flynn and Wall and "Model-free Kinetics" models require at least three dynamic curves with different heating rates, the following were used: 10, 20 and 30 °C min^{-1} between room temperature and 700 °C. The mass of the powder was approximately 1 mg, the powder support was alumina, and the carrier gas was synthetic air with a flow of 50 mL min^{-1}.

2.3. Kinetic methods

The ASTM E1641 standard determination of kinetic parameters via thermogravimetry is based on methods proposed by Flynn and Wall [6] and "Model-free Kinetics" [7–9] that are models based on the isoconversion principle, which states that a constant conversion (α) of the reaction rate is only a function of temperature, and allow determination of the kinetic parameters of a reaction, as activation energy, by thermal analysis. In the typical experiments is necessary to obtain least at three different heating rates (β) and plotting ln (α) against $1/T$ giving straights lines with slopes $-E_\alpha/R$. The Flynn and Wall kinetic model is an iterative method that uses linear regression to determine the slope and "Model-free Kinetics" is an integral method which allows to evaluate both simple and complex reactions. These methods were used to evaluate which one best fits to determine the apparent activation energy for decomposition gelatin bound to metal ions of the system as a parameter for characterizing and optimizing the conditions of synthesis and applicability of these materials. These models were used to determine the apparent activation energy (Eq. (1)) and conversion (α) as a function of temperature.

$$\ln\frac{\beta}{T_\alpha^2} = \ln\left[\frac{RA}{E_\alpha g(\alpha)}\right] - \frac{E_\alpha}{R_\alpha}\frac{1}{T_\alpha} \quad (1)$$

Fig. 1 illustrates obtaining the activation energy and pre-exponential factor from the Arrhenius curve (linear regression). As the equation of the line $y = a_0 + a_1x$ we have, by linear regression fits the best straight line $y = a_0 + a_1x$. Thus it have:

$$\alpha_o = \ln\left[\frac{RA}{E_\alpha g(\alpha)}\right] e a_1 = \frac{-E_\alpha}{R} \quad (2)$$

From Eq. (2) it possible obtain $E_\alpha = -R{\cdot}a_1$.

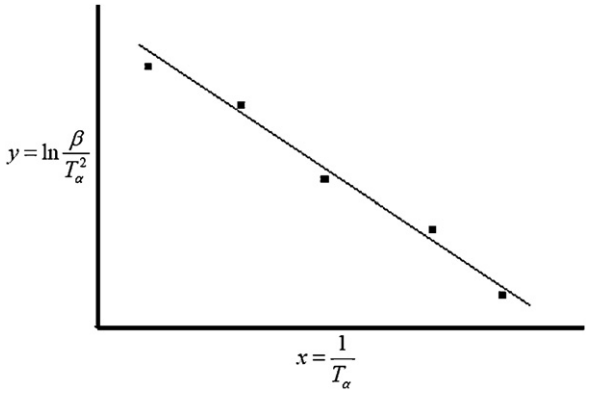

Fig. 1. Curve Arrhenius.

3. Results and discussion

The thermogravimetric curves (TG) of the $PrCoO_3$ and $PrNiO_3$ powders, are represented in Fig. 2. Also in Fig. 2c was observed that the decomposition of the gelatin and the precursor powders occurs in three distinct steps. The first step, which corresponds to a reduction of 12.2%, is associated to humidity (hydration water). The second, around 44.4%, can be attributed to the elimination of amino acid fragments, usually proline, which is thermodynamically susceptible to thermal degradation in oxidant atmosphere. The last step, with mass loss of around 41.4%, may be associated to glycine degradation [10]. Decomposition occurs at higher temperatures for precursor powders, owing to the glycine interaction by means of the carboxylate groups and amine with the metal ions forming the coordination groups, thereby providing more stability to the structure and avoiding the oxidation of a large amount of glycine.

The differential thermal analysis curves of the precursor powders (Fig. 3) show a sharp exothermal peak in the 300–450 °C range. This peak can be attributed to the decomposition processes of the organic groups and the rupture of bonds between the metal ions and carboxyl groups of the organic template [10].

The crystallization of the $PrCoO_3$ powder, revealed in Fig. 4, is complete at 700 °C, with the formation of species with $PrCoO_3$ perovskite-type structure at a higher proportion and a number of Co_3O_4 spinel phase peaks. The results illustrated in Fig. 5 show the diffractograms of the $PrNiO_3$ powder, with complete crystallization of $PrNiO_3$ structure at 700 °C and isolated oxides such as Pr_6O_{11} and NiO. According to the Escote et al. [11], $PrNiO_3$ monophasic

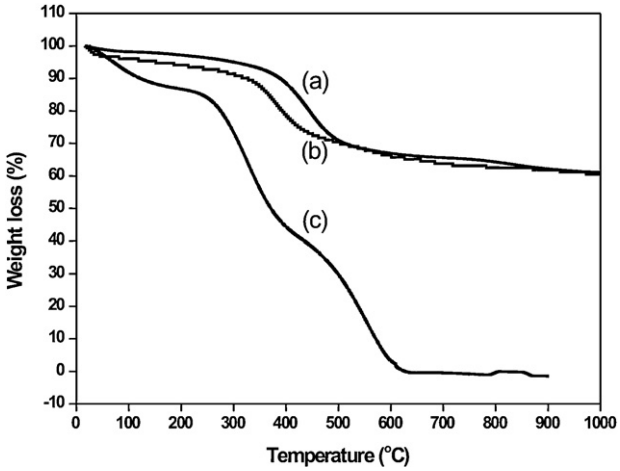

Fig. 2. Thermogravimetric curves of powders (a) $PrCoO_3$, (b) $PrNiO_3$ and (c) gelatin.