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Combustion Syntheses of Co_3O_4 Powders Using Different Fuels

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Abstract

Co_3O_4 powders are used as pigment in solar selective paints. In this work, two new gel-combustion processes for the synthesis of Co_3O_4 nanopowders with lysine (Lys) or ethylenediaminetetraacetic acid (Edta) as fuel are presented. The first route is a conventional, stoichiometric process, while the second one is a non-stoichiometric, pH-controlled process. The samples were calcined in air at 500 ºC. They were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectrum (FTIR), Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) and the optical properties of the pigments were assessed with a spectrophotometer. In all cases, powders exhibited the Co_3O_4 crystalline structure. A minimum crystallite average size of 19 nm for powders obtained by the "stoichiometric/Lys" combustion route was observed, meanwhile, a maximum value of 47 nm was stated for powders obtained by the "non-stoichiometric/Edta" combustion process. The average particle size ranged between 50 and 100 nm. The powders obtained by the stoichiometric nitrate–lysine route were selected to study its optical properties, their solar absorption was 88%, compared with the references, evidencing their aptitude to be used in solar absorbent paints.

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1. Introduction

The oxides of transition metals (Co, Mn, Fe, Cr), for example Co_3O_4, present a high absorption in the solar spectrum by the existence of numerous, allowed, electronic transitions between their "d" orbitals partially full (Vince et al., 2000). The cobalt pigments are of paramount importance in ceramic industry due their spectacular variety of colors, high tinting strength and remarkable stability under chemical, thermal and reducing conditions (Mimani and Ghosh, 2000). Thus, cobalt oxides are used in absorbent paints to solar collector between other applications like gas-sensing, catalysis and anode material in Li-ion rechargeable batteries (Yang et al., 2010). Co_3O_4 has been obtained by different methods as, precipitation (Pal and Chauhan, 2010), sol-gel (Luisetto et al., 2008), spray-pyrolysis (Avila et al., 2004), hydrothermal synthesis (Gui et al., 2012). Other methods like, reflux (Ozkaya et al., 2009), macanochemical (Yang et al., 2004), ultrasound assisted (Askarinejad and Morsali, 2009), on biotemplates (Yang et al., 2010) and chemical vapor deposition (CVD) (Barreca et al., 2011) using organic complexes (Thangavelu et al., 2011) and by gel-combustion synthesis (Venkateswara and Sunandana, 2008- Toniolo et al., 2010) were also viable.

In particular, in gel-combustion synthesis of Co_3O_4, it has been studied the influence of fuel-oxidant ratio and fuel types on powders properties. For example in studies of combustion syntheses using urea as fuel, it was achieved an optimized fuel-oxidant ratio which allowed a smallest average crystallite size of 6 nm (Venkateswara and Sunandana, 2008). On the other hand, both the influences of type of fuels and fuel-oxidant ratio were studied in Co_3O_4 powders obtained by combustion syntheses using urea and glycine as fuels, in these studies the smaller average size of crystallite was 23 nm and the largest specific surface area was $36 m^2/g$ using glycine as fuel.

In this work, two new gel-combustion routes for the synthesis of Co_3O_4 nanopowders with lysine (Lys) or ethylenediaminetetraacetic acid (Edta) as fuels are presented. The first route is a conventional stoichiometric process, while the second one is a non-stoichiometric, pH-controlled process. The samples were calcined in air at 500 ºC. They were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared spectrum (FTIR), Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and the optical properties of the pigments were assessed with a spectrophotometer.

The objective of this work is to establish the influence of the type of fuel and the synthesis route on the final properties of obtained powders like crystalline structure, average crystallite size and shape and size of particle, and to verify the aptitude of powders to be used for solar selective paints.

2. Experimental Procedure

Co_3O_4 nanopowders were obtained by gel-combustion process for the synthesis using Lys ($C_6H_{14}N_2O_2$) or Edta ($C_{10}H_{16}N_2O_8$) as fuels. The first one is a conventional stoichiometric process, while the second one is a non-stoichiometric, pH-controlled process. All the chemical routes were performed using reagents of analytical grade. The final calcination temperatures were at 500 ºC during 2 h.

2.1. Stoichiometric processes

Stoichiometric nitrate–lysine route

5g of $Co(NO_3)_2.6H_2O$ (Aldrich) and 0.83g of Lys ($C_4H_7NO_4$,Aldrich) were dissolved in distilled water to obtain a homogeneous solution, with a total volume of 250 ml (pH 3). The Lys/Co molar ratio chosen was 9/34(0.26) as calculated on the basis of the following stoichiometric reaction of combustion:

$$34\ Co(NO_3)_2.6H_2O + 9\ C_6H_{14}N_2O_2 \rightarrow 17\ Co_2O_3 + 54\ CO_2 + 267\ H_2O + 43\ N_2 \quad (1)$$

This precursor solution was concentrated on a hot plate at 250 ºC until a viscous gel was obtained. Soon after, it ignited and the combustion process proceeded without flame. These powders were named Co_3O_4-S-Lys.

Stoichiometric nitrate–Edta route:

The same procedure was used, starting from the same mass of 5g of $Co(NO_3)_2.6H_2O$, but in this case the stoichiometric reaction requires an Edta/Co molar ratio of 9/40(0.22), based on the following, stoichiometric reaction of combustion:

$$40\ Co(NO_3)_2.6H_2O + 9\ C_{10}H_{16}N_2O_8 \rightarrow 20\ Co_2O_3 + 90\ CO_2 + 312\ H_2O + 49\ N_2 \quad (2)$$

These powders were named Co_3O_4-S-Edta.

2.2. Non-stoichiometric, pH-controlled process

Non-stoichiometric pH-controlled nitrate–lysine route

A first solution was prepared from 5g of $Co(NO_3)_2.6H_2O$ (Aldrich), 10ml of HNO_3 (concentrated) and an amount of distilled water sufficient to reach a volume of 100ml. This solution was concentrated until a small volume in a hot plate to reduce the amount of nitrates, and then distilled water was added again to obtain 100 mL of solution. A second solution was prepared by dissolving 4.15g of Lys in distilled water. Then, both solutions were carefully mixed, resulting the homogeneous mixture with a Lys/Co molar ratio of 1.32. This ratio was chosen based on the "oxidative valence criterion", taking into account previous studies of similar processes, where the optimum ratio for a pH controlled nitrate–glycine route to synthesize ZrO_2–CeO_2 solid solutions was found to be 5 (Jain et al., 1981-Lascalea 2004). Then, NH_4OH (diluted 1:1, Merck) was added to obtain a precursor solution with pH 8. This solution was then concentrated on a hot plate at 250 ºC until it turned into a viscous gel, which finally burned with flames due to the desired, exothermic reaction of combustion. These powders were named Co_3O_4-NS-Lys.

Non-stoichiometric pH-controlled nitrate–Edta route:

The same procedure was used, starting from the same mass of 5g of $Co(NO_3)_2.6H_2O$, but in this case also based on of above-mentioned criterion, the Edta /Co molar ratio resulted of 1.12. These powders were named Co_3O_4-NS-Edta.

2.3. Materials characterization

The phases present in the as-synthesized Co_3O_4 nanopowders (obtained after calcination) were identified by X-ray diffraction (XRD) using a Philips PW 3710 diffractometer operated with Cu-Kα radiation. Our data were compared with those reported in the Inorganic Crystal Structure Database (ICSD). The average crystallite size was determined from the broadening of Bragg peaks using the Scherrer equation (Klug and L. Alexander, 1974).

The morphology of the powders was analyzed by scanning electron microscopy (SEM, Philips 505 microscope) and transmission electron microscopy (TEM, JEOL 100 CX II microscope). The operation voltage was 100kV. In both cases, the preparation of samples was performed following conventional procedures.

Fourier transform infrared spectrum (FTIR) of powders was obtained with a Bruker IFS 66 equipment. TGA (Thermogravimetric Analysis) was carried out with a detector SHIMADZU TGA-51 type at a rate of 20ºC/min, between environmental temperature and 600 ºC, in air, with a platinum cell. DSC (Differential Scanning Calorimetry) was carried out with a detector SHIMADZU DSC-50 type at a rate of 20ºC/min, between environmental temperature and 600ºC in air, with an aluminium cell.

The optical characteristics, transmission and reflection of samples in the solar spectrum, were studied with a spectrophotometer of double beam SHIMADZU, model UV-3101PC with integration sphere model 3100. From this measures it was calculated the solar absorptance (α_S). The studied pigments were placed in a basin of quartz.

3. Results and discussion

In agreement with the XRD pattern of Fig. 1, a spinel crystal structure of Co_3O_4 corresponding to database ICSD N° 36256, was obtained in all obtained powders. The average crystallite sizes calculated by Scherrer´s equation are informed in Table 1, evidencing that a minimum crystallite average size of 19 nm was observed for powders obtained by the "stoichiometric/Lys" combustion route, meanwhile, a maximum value of 47 nm was stated for powders obtained by the "non-stoichiometric /Edta" combustion process. Additionally powders, obtained by stoichiometric routes, had lower average crystallite sizes than those obtained by non-stoichiometric processes, since similar tendencies are observed in Co_3O_4 powders synthetized by combustion syntheses using glycine and urea as fuels (Toniolo et al., 2010) and in $Ce_{0.9}Zr_{0.1}O_2$ powders obtained by gel-combustion methods using different fuels (M.G. Zimicz et al., 2011). The influence of the type of fuel is, then, evident over the observed crystallite average size, being lowest these powders obtained by Lys routes.

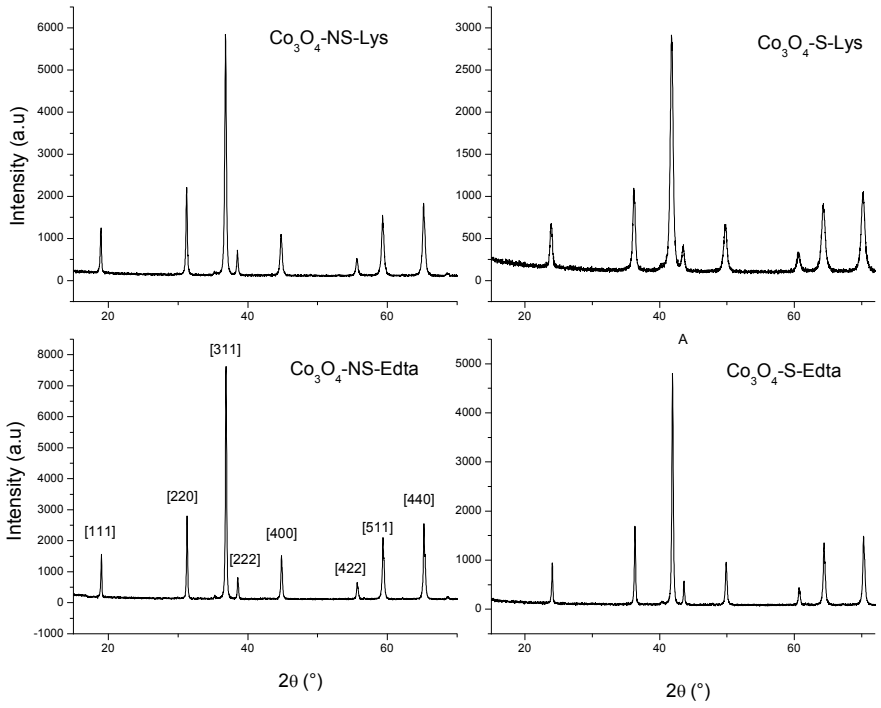

Fig. 1. XRD patterns of Co_3O_4 obtained nanopowders.

Specific surface areas of obtained Co_3O_4 powders are exhibit in Table 1, the higher area corresponding to Co_3O_4-NS-Edta powders. Additionally the specific surface area of powders obtained using Edta as a fuel is higher than the observed from powders obtained with the same route employing lysine as fuel.

Table 1. Average crystallite sizes and BET specific surface areas of obtained Co_3O_4 nanopowders.

Route	Average crystallite size (nm)	BET specific surface area (m^2/g)
Co_3O_4-S-Lys	19	13
Co_3O_4-NS-Lys	38	8
Co_3O_4-S-Edta	43	23
Co_3O_4-NS-Edta	47	29

By SEM, it was observed that all samples exhibited a high degree of agglomeration, as is shown in Fig. 2. In particular, for powders obtained by non-stoichiometric routes, structures more compact are observed. A similar agglomeration is evidenced in Co_3O_4 powders synthetized by combustion synthesis using glycine and urea as fuels (Venkateswara and Sunandana, 2008).

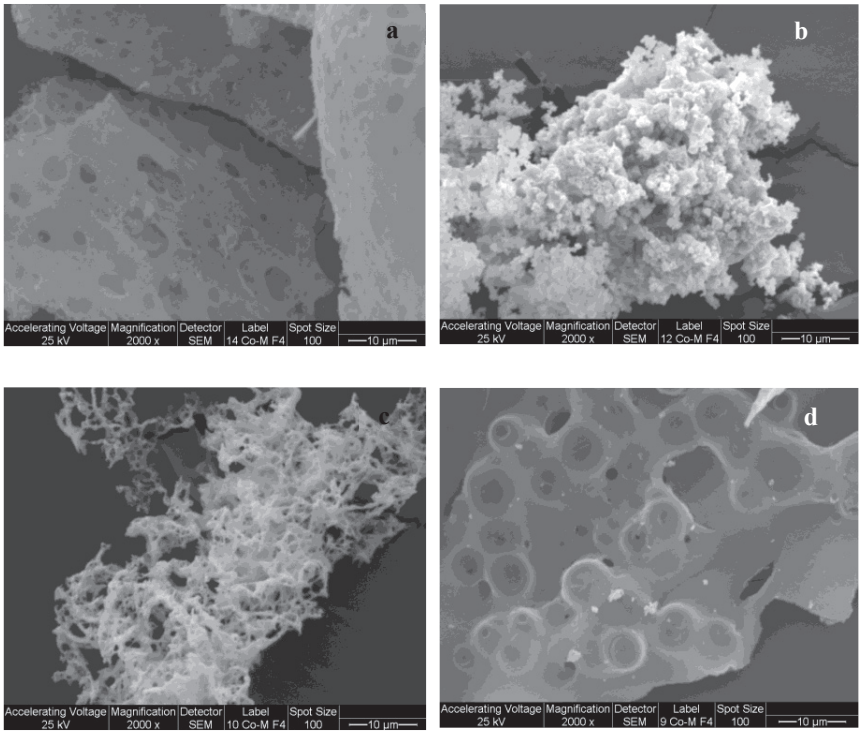

Fig 2. SEM micrographs of: a) Co_3O_4-S-Lys, b) Co_3O_4-NS-Lys, c) Co_3O_4-S-Edta and d) Co_3O_4-NS-Edta.

As can be estimated through TEM observations, the agglomerated particle size ranges between 50 and 100 nm, as shown in Fig. 3, where are displayed TEM micrographs of all obtained powders. A polyhedral shape of crystallites

is evidenced as well, with an octahedral shape more frequently observed. The same shape was observed in Co_3O_4 particles obtained by precipitation methods too (Tang and Hao, 2008).

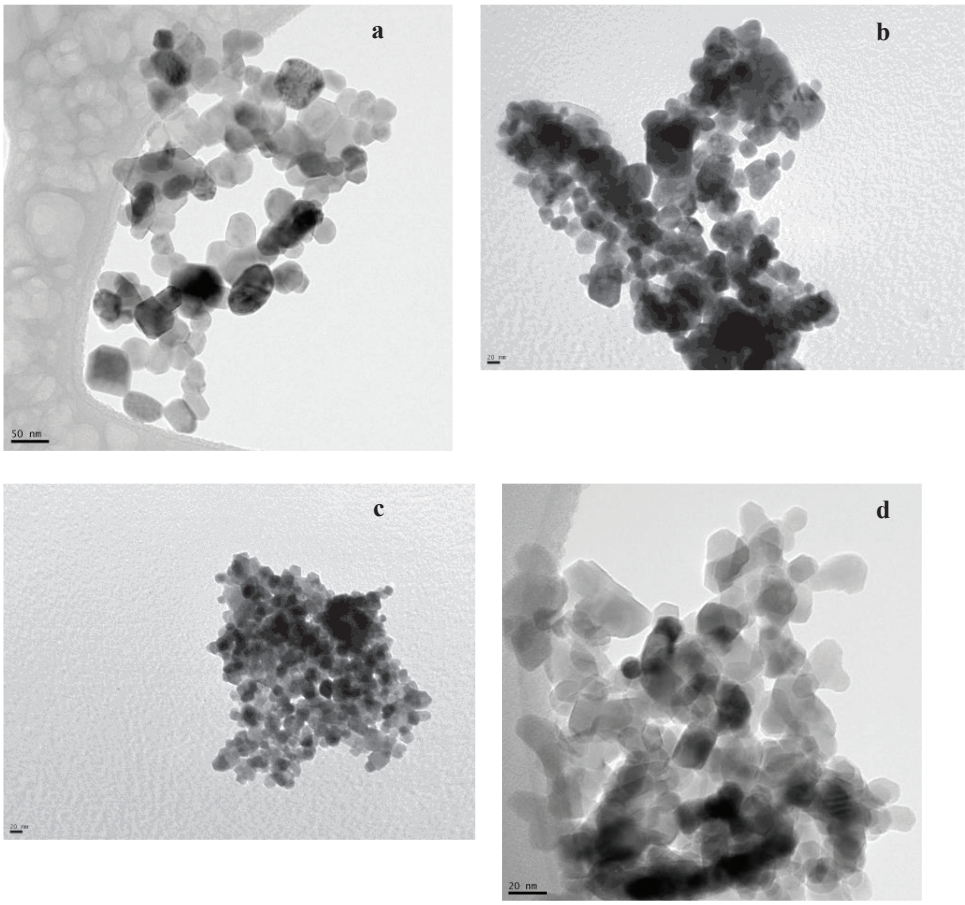

Fig 3. TEM micrographs of: a) Co_3O_4-S-Lys, b) Co_3O_4-NS-Lys, c) Co_3O_4-S-Edta and d) Co_3O_4-NS-Edta.

DSC and TGA plots corresponding to Co_3O_4-NS-Edta can be observed in Fig. 4. At 400°C an exothermic transformation with a release of energy of 36 mW was observed. Additionally a loose of weight of 0.05 mg was produced at the same temperature. Both changes could be related with a phase change from the CoO phase to Co_3O_4 phase according to the phases found by Toniolo et al. (2010), like Co, CoO and Co_3O_4, in ashes collected after a combustion synthesis of cobalt oxides.

FT-IR were carried out on samples of all the obtained powders, all resulting spectra were identical to the one plotted in Fig. 5. The IR spectra evidenced two distinct and sharp bands at 622(ν_1) and 727 (ν_2) cm^{-1}, which originate from the stretching vibrational modes of the metal–oxygen bond and confirming the formation of a Co_3O_4 spinel oxide. The ν_1 band is characteristic of Co^{3+} vibration in octahedral sites of the spinel, and ν_2 band is attributable to Co^{2+} vibration in tetrahedral ones (Gui et al., 2012). Similar bands corresponding to ν_1 y ν_2 are observed in cobalt oxides synthetized by microwave methods (Al-Tuwirqi, 2011).

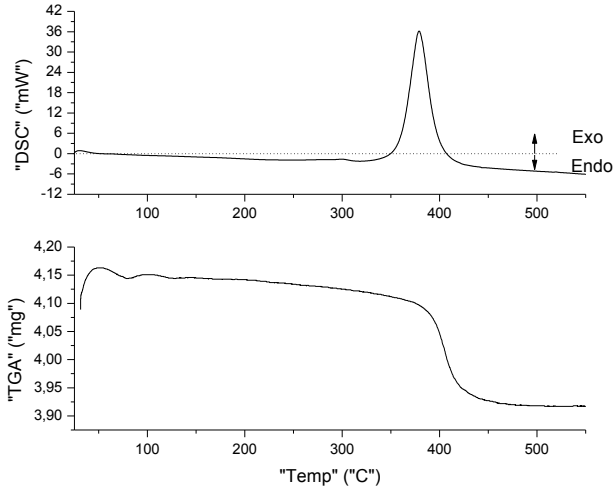

Fig 4. DSC y TGA plots of Co_3O_4-EC-Edta.

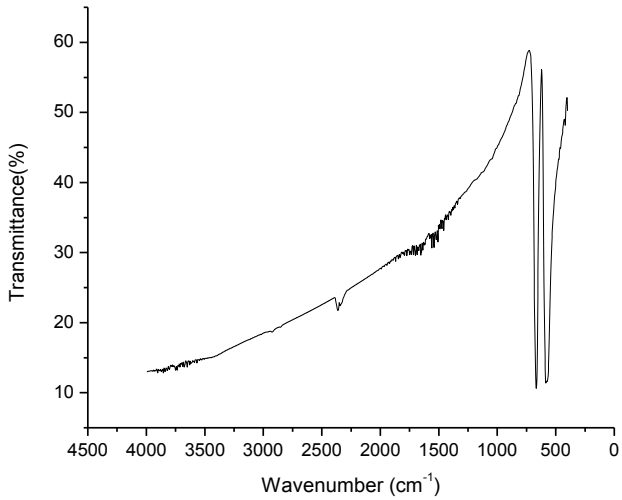

Fig. 5. FT-IR Spectrum of Co_3O_4-NS-Lys.

Among the four nanopowders obtained, the Co_3O_4-S-Lys ones were selected to study their optical properties with a spectrophotometer, because the observed efficiency of their synthesis was the best, stated in terms of the mass of

produced pigment. The objective of this study was to verify their optical properties before the fabrication of the solar paints. The resulting solar absorption was 88 %. These results evidence their aptitude to be used in solar absorbent paints because the absorption is just in the range of 88-94%, usually acceptable for generic solar selective paints made with pigments of Co_3O_4 (Van Buskirk, 1982).

4. Conclusion

In this work, two new gel-combustion processes for the synthesis of Co_3O_4 nanopowders, with lysine (Lys) or ethylenediaminetetraacetic acid (Edta) as fuel are presented. The first route is a conventional, stoichiometric process, while the second one is a non-stoichiometric, pH-controlled process. A spinel crystal structure of Co_3O_4 was observed in all obtained powders. A minimum crystallite average size of 19nm for powders obtained by the "stoichiometric/Lys" combustion route was observed, meanwhile, a maximum value of 47nm was stated for powders obtained by the "non-stoichiometric /Edta" combustion process. Additionally, that powders obtained by stoichiometric routes yield lower average crystallite sizes than the obtained by non-stoichiometric processes was confirmed as a rule in this material. The influence of the type of fuel is evidenced on crystallite average size, being the lowest values observed on powders obtained by means of the Lys routes. By TEM the size particle of agglomerates was evaluated ranging 50-100nm, being the crystallites polyhedral shaped as observed. The nanopowders obtained by stoichiometric nitrate–lysine (the process with the best yield) were selected to study optical properties. Their solar absorption was 88% evidencing their aptitude to be used in solar absorbent paints, as compared with other related pigments descripted in literature.

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