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Combustion synthesis of Co_3O_4 nanoparticles: fuel ratio effect on the physical properties of the resulting powders

M. C. Gardey Merino[a]*, M. Palermo[a], R. Belda[a], M. E. Fernández de Rapp[c], G. E. Lascalea[b] & P. G. Vázquez[d]

[a]*Grupo CLIOPE, Universidad Tecnológica Nacional - Facultad Regional Mendoza, Rodríguez 273, Mendoza-5500, Argentina.*

[b]*Laboratorio de Investigaciones y Servicios Ambientales Mendoza (LISAMEN) - CCT CONICET– Mendoza, Av.Ruíz Leal s/n Parque General San Martín, Mendoza-5500, Argentina.*

[c]*Centro de Investigaciones en Sólidos (CINSO) CITEDEF – CONICET, J.B. de La Salle 4397, Villa Martelli, Prov. de Buenos Aires (B1603ALO), Argentina.*

[d]*Centro de Investigación y Desarrollo en Ciencias Aplicadas "Dr. Jorge J. Ronco" (CINDECA) CCT CONICET – La Plata, Universidad Nacional de La Plata, Calle 47 N° 257 La Plata-1900, Buenos Aires, Argentina.*

Abstract

Co_3O_4 nanoparticles have been obtained by stoichiometric combustion synthesis: in particular 4 nitrates-aspartic routes each with different fuel ratio (ranging 0.5-2.5) have been studied. It has been determined through XRD that the crystalline structure present in all obtained powders was the face-centered cubic corresponding to Co_3O_4 and it has been evaluated an average crystallite size ranging between 21 and 76 nm. As regards to the effect of fuel ratio on physical properties, an increment on the crystallite average size and a drop on the specific surface area with the increase of the fuel ratio has been observed.

Keywords: Co_3O_4 nanoparticles; combustion synthesis; fuel ratio; aspartic acid.

* Corresponding author. Tel.: +542615243001; fax: +542615244531.
E-mail address: mcgardey@frm.utn.edu.ar.

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1. Introduction

The Co_3O_4 has drawn extra attention due to their broad range of applications in solid-state sensors, electrochromic devices, heterogeneous catalysts, lithium–ion batteries and solar energy absorbers (Lun-Hong et al., 2009). Solar absorber coatings have attracted a great deal of interest, because the efficiency of any solar collector system is strongly dependent on the ability of its absorber to convert solar radiation into heat (Vince et al., 2003). An absorber coating is generally composed of metallic substrates covered by absorber paints. Mixed oxides, and simple oxides like Co_3O_4 (Buskirk, 1982) are generally used like pigments in these paints. The pigments are based on various transition-metal oxides as Mn, Co, Fe and Cr because of their high absorption levels across the whole solar radiation spectrum; the reason is the existence of numerous spin-allowed electron transitions between partially filled d-orbitals (Vince et al., 2003). Pigments like Co_3O_4 are synthesized by different methods like microwave-assisted combustion method (Lun-Hong et al., 2009), mechanochemical synthesis (Yang et al., 2004), precipitation methods (Buskirk, 1982, Pal et al., 2010) but by gel-combustion synthesis there are few references, for example cobalt oxides powders are obtained by urea and glycine-nitrates routes (Toniolo et al., 2010) and, actually, continuous and controllable combustion synthesis has been also studied (Chong-hu, 2011). The effect of fuel to oxidizer molar ratio on structure and microstructure has been analyzed too (Venkateswara Rao et al., 2008). In this work, it has been obtained Co_3O_4 nanoparticles by stoichiometric combustion synthesis, in particular by aspartic-nitrate routes. The effect of a fuel ratio (n(Asp)/n(Co)) ranging between 0.5 and 2.5 of physical properties of obtained powders was analyzed. The obtained powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and their textural properties have been determined employing our Brunauer-Emmett-Teller isotherms. The effect of fuel ratio on physical properties like the average crystallite size, the specific surface area and the morphology of obtained powders has been studied too. Obtained powders in this work will be used as pigments in solar absorber paints.

2. Experimental procedures

2.1. Materials synthesis

In a beaker 1,37g of aspartic acid ($C_4H_7NO_4$, Fluka) and 5g of cobalt nitrate ($Co(NO_3)_2.6H_2O$, Aldrich) were dissolved in distilled water by heating and stirring on a hot plate (HP), resulting in a precursors solution with a pH=3. Finally, this solution was thermally concentrated on a HP at 250°C. In the process, a violet gel was formed, which, at a critical dryness began to burn acquiring the appearance of embers. A sparkling combustion without flame was observed. The resulting ashes were calcined in an open-air oven at 500°C during 2 hours to get rid of carbonaceous residues and to obtain the desired crystalline structure. The powder obtained by this method will be referred as Co_3O_4 (fuel ratio 0.6) or powder from the stoichiometric process: the proper amounts of precursors for this synthesis was determined by the following, stoichiometric reaction:

$$10\ Co(NO_3)_26H_2O + 6\ C_4H_7NO_4 \Rightarrow 5\ Co_2O_3 + 24\ CO_2 + 81\ H_2O + 3\ N_2 \quad (1)$$

In order to study the effect of fuel-to-oxidant-ratio on the chemical composition, average crystallite size, specific surface area, and morphology, similar aspartic-nitrate routes were carried-out with different fuel ratio of 0.5, 1.5 and 2.5.

2.2. Characterization of Co_3O_4 nanopowders

The crystalline phases of obtained powders and their respective average crystallite sizes were studied by a Philips PW 3710 equipment operated with Cu-Kα radiation. The average crystallite sizes were calculated from Bragg´s peaks using Scherrer´s equation (Klug et al., 1974). The surface morphology of powders was observed by SEM (Philips 505). Additionally, by TEM (JEOL JEM-2010) average sizes and morphology of obtained powders were determined. The experimental procedure to observe these specimens in TEM is the following: a film of acetate/butyrate is placed over the usual, grid type, sample holder and dissolved in ethyl acetate. In order to form holes, drops of glycerin were placed, and finally a carbon film is deposited to improve the mechanical resistance. The specific surface areas of the powders were measured by the multipoint Brunauer-Emmett-Teller (BET) adsorption technique using a Micrometrics Accusorb 2100E equipment.

3. Results and discussion

Face centered cubic crystalline structure corresponding to a spinel crystal structure of Co_3O_4, in accordance to data base ICSD N° 36256, were identified in all obtained powders. Obtained X-ray diffraction spectra for both Co_3O_4 (fuel ratio 0.6) and Co_3O_4 (fuel ratio 2.5) were shown in fig. 1.

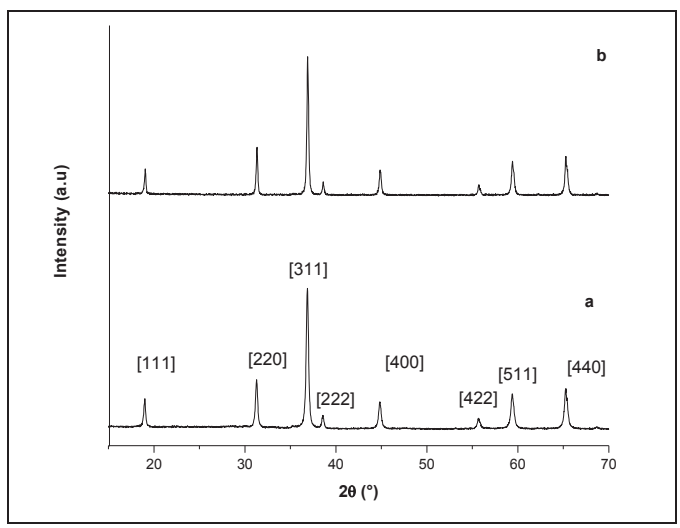

Fig. 1. XRD diffraction patterns: where “a” corresponds to a powder of Co_3O_4 obtained with a fuel ratio of 0.6 and “b” belongs to that powder obtained with a 2.5 fuel ratio.

Average crystallite sizes and BET specific surface area of obtained powders corresponding to different fuel ratio are listed in table 1. Regarding this empirical frame, a definite effect of the fuel ratio on average crystallite size is observed: for a fuel ratio of 0.5 was observed the lowest average crystallite size of 21 nm, this average size increases with the growing of fuel ratio value until 1.5, but, from this point, reaching the highest value of fuel ratio essayed (2.5), the average crystallite seems to remain unchanged within a reasonable experimental error. From a thermodynamical point of view, when fuel ratio is incremented, temperature of flame and the average crystallite size increases as well (Toniolo et al., 2010). In this work this

tendency is generally observed but it will be necessary to increase the number of experiences to confirm it. Co_3O_4 particles has been obtained by thermal methods were average crystallite sizes of 35 nm has been determined (Wang et al., 2004), this value is higher than powders obtained from synthesis with 0.5 and 0.6 fuel ratio values. For another hand, in ashes produced by combustion synthesis in particular in urea-nitrate routes the lowest average crystallite size has been determined for a specific fuel quantity (Venkateswara Rao et al., 2008). With the aim of finding the lowest average crystallite size corresponding to aspartic-nitrate routes it is necessary to carry-out a parametric study in the future. The effect of crystallite size on optical properties of Co_3O_4 particles has been analysed (Feng et al., 2007); this effect could cause a variation of solar absorbance in powders of Co_3O_4 that composes the solar absorber paints. Additionally, as generally expected, for BET specific surface area values dropping in the range of 25 to 8 m^2/g, the corresponding average crystallite size values are gradually increasing (21 nm to 76 nm), being the 66 nm value disregarded in this discussion, since it is almost indistinguishable, within the experimental error, of the 76 nm one.

Table 1. Physical properties of powders obtained from different fuel ratio based syntheses: Average crystallite size and BET specific surface Area.

Fuel ratio n(Asp)/n(Co)	Average crystallite size (nm)	BET specific surface area (m^2/g)
0.5	21±2	25±2
0.6	46±5	20±2
1.5	76±8	8±1
2.5	66±7	11±1

As an example, two SEM´s micrographs taken from selected specimens of our powders are shown in fig. 2. In these cases (as in general), agglomerates of particles with micrometric pores are observed. It is worth to mention that similar morphologies are present in Co_3O_4 powders synthetized by others combustions methods (Chong-hu, 2011).

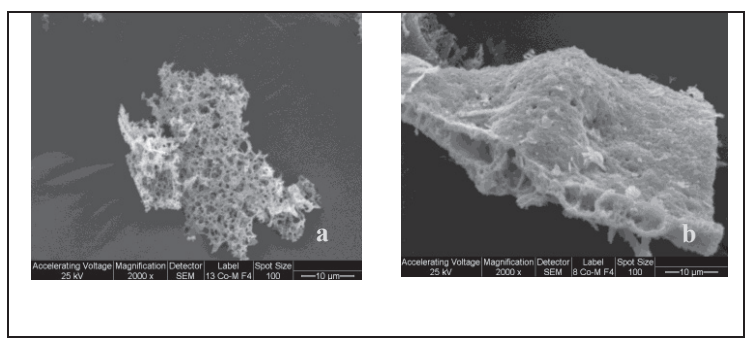

Fig. 2. Two SEM micrographs for Co_3O_4 powders obtained with a fuel ratio: (a) 0,5 and (b) 2.5.

In TEM micrographs of all powder specimens shown in fig. 3, are observed particles with an average particle size ranging between 20 and 100 nm, reasonably matching with the indirect average crystallite size

calculated by means of Scherrer´s equation. Additionally, polygonal particles with octahedral shape are seen, the same shape was seen in Co_3O_4 synthesized by precipitation-reduction route (Tang Xingfu et al., 2008).

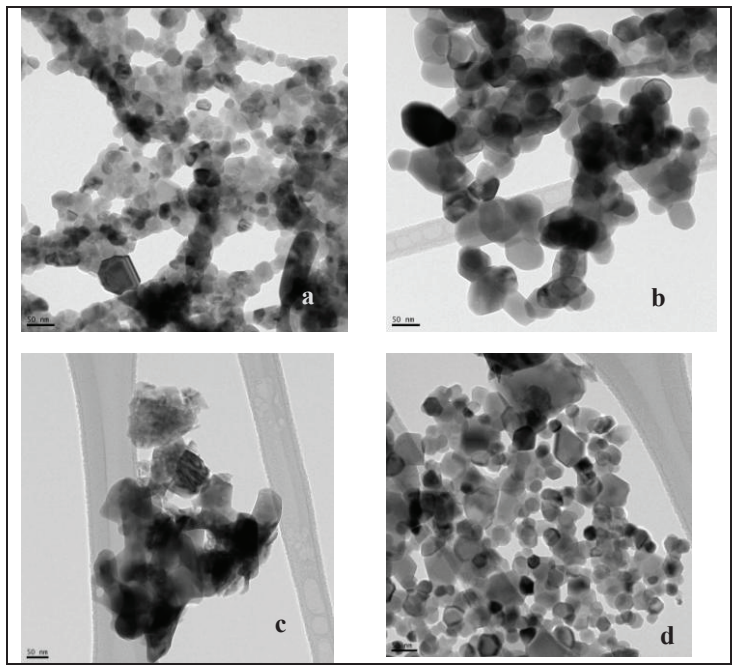

Fig. 3. TEM micrographs for Co_3O_4 powders obtained with all fuel ratios examined: (a) 0.5, (b) 0.6, (c) 1.5 and (d) 2.5.

4. Conclusions

Co_3O_4 powders were synthesized by four combustion syntheses, aspartic-nitrates routes where different fuel ratios ranging between 0.5 to 2.5 were used. By direct measuring on TEM micrographs, the average size of particles/crystallites was ranging between 20 and 100 nm, and calculated by means of Scherrer´s equation they ranged between 20 and 80 nm, in good agreement.

When the fuel ratio is incremented, average crystallite size is incremented too, however this tendency doesn't result full conclusive (especially for the most rich combustible process) and the tendency might be confirmed with more experimental work in future studies.

Additionally, it was generally seen that specific surface area is incremented when average crystallite size is diminished. With the aim of finding the lowest average crystallite size corresponding to these aspartic-nitrate combustion routes, it will be necessary to carry-out a parametric study in future work.

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