Investigating of Thermal Stability of 2D and 3D CoAl₂O₄ Particles in Core-Shell Nanostructures by Raman Spectroscopy.

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ABSTRACT

We are studying the formation of a nanostructured spinel CoAl₂O₄ layer on α -Al₂O₃ giving rise to a core-shell composite. In the final product, two mechanisms of CoAl₂O₄ crystallization onto a α -Al₂O₃ microparticle surface are observed, depending on the dispersion grade of Co₃O₄: a 3D nanostructure from the arrangement of Co₃O₄ agglomerated nanoparticles; 2D nanoparticles from the diffusion mechanism of isolated Co₃O₄ nanoparticles. As a consequence, two different crystallization pathways may occur during the thermal treatment. In order to understand the formation mechanisms a Raman Confocal Study is performed. The features of the Raman spectra of the samples depend strongly on the morphology of the nanoparticles located in the shell of the microparticle. Average spectra of the samples show a variation in the Raman shift between the different samples. The differences between 3D or 2D structures is associated with the transmission of phonons among the nanoparticles. The high absorbance of the cobalt species could mask the Raman shift displacement by local heating, so both the temperature and the laser source power are considered in the Raman study. The evolution of the Raman spectra with applied temperature indicates a decoupling of the Raman modes. This fact is more relevant for the 3D aggregates in which nanoparticles produced a larger scattering of phonons and a higher sensitivity to temperature variation. These

results clearly indicate that extrinsic parameters such as the size of the crystals and their aggregation state affects their Raman properties.

INTRODUCTION

At nanoscale, materials often possess physical and functional properties that are dramatically different from their corresponding bulk crystals [1]. This is one of the main reasons why the research on nanoscale materials; such as nanowires, nanoparticles and quantum dots; has made great progress in the last few years. For practical applications, nanomaterials are integrated into heterostructures [2] or dispersed into different supports. One of the approaches that is useful to nanoparticles is the use of a core-shell type nanostructure that corresponds to biphasic materials, which have an inner core and an outer shell made of different components. These particles are of interest, as they can exhibit unique properties arising from the combination of dissimilar core and shell materials, geometry and design [3–5]. Several techniques have been investigated for depositing nanoparticles onto the cores, including seed methods [6], thermal evaporation techniques [7], self-assembly methods [8], electroless plating [9], sol-gel methods [10], molten salts synthesis [11] and dry-dispersion procedures [12–14].

In a recent study, dry-dispersion of CoAl_2O_4 nanoparticles onto $\alpha\text{-Al}_2\text{O}_3$ microparticles with a further thermal treatment showed two different pathways for CoAl_2O_4 crystallization [15]. Materials with different nanostructures are formed depending on the dispersion grade of Co_3O_4 : 3D nanostructure regions from the arrangement of Co_3O_4 agglomerated nanoparticles; 2D nanoparticles from the diffusion mechanism of isolated Co_3O_4 nanoparticles [15]. Therefore,

the difficulties in characterizing these types of compounds are a current challenge in understanding nanostructured materials [16].

Attached to the appearance of unusual functional properties, the crystalline parameters are able to be modified at nanoscale. However, the structural studies at nanoscale are complex and require high-resolution techniques. Generally speaking, common techniques with enough resolution to determine structural parameters in nanometric materials are X-Ray Diffraction (XRD) and Transmission Electron Microscopy (TEM). However, in the case of core-shell nanostructured microparticles, there are limitations in the structural analysis of nanoregions because of the appearance of multiple phases, interface phenomena, agglomeration state or even simply the limited resolution of the techniques. The problem to be addressed is to combine the structural and microstructural characterization in a single procedure. Confocal Raman microscopy is a powerful non-destructive technique with high spectral and spatial resolution that is able to resolve structure–microstructure of a wide variety of materials and composites [17–19]. Raman spectroscopy reveals information about the crystal structure, electronic structure and lattice vibrations; it can be used to probe thickness, strain, structural stability, defects or charger effects. For these reasons, it is an efficient tool for the characterization of 2D materials [20].

Therefore, the aim of this work is to differentiate among dissimilar nanostructures in a core-shell microparticle by using Confocal Raman Spectroscopy. Both 2D particles and 3D nanostructures have the same composition, CoAl_2O_4 , which presents high laser absorption and is therefore suitable for heating. We look at the differences in Raman spectra related to the

shell CoAl_2O_4 nanoparticles on $\alpha\text{-Al}_2\text{O}_3$ core microparticles. In addition, the nature of the 2D and 3D nanoparticles affects the phonons' density through the transmission and reflection processes of phonons, showing that particle-to-particle interphases modify the thermal response of the nanostructure.

Raman spectra of CoAl_2O_4 .

CoAl_2O_4 is a normal spinel, which exhibits a cubic structure, with $\text{Fd}3\text{m}$ space group ($Z = 8$). In this structure, the oxygen anions form a cubic close-packed (ccp) sub-lattice surrounded by Co^{2+} and Al^{3+} cations occupying tetrahedral and octahedral sites, respectively. The cations occupy only $\frac{1}{8}$ of the tetrahedral sites (8a Wyckoff position) and $\frac{1}{2}$ of the octahedral sites (16d Wyckoff position) [21]. Anisotropy of the surface energy provokes CoAl_2O_4 into adopting a face-centred cubic crystal structure, and the general sequence for the surface energies of the spinel structure is $\gamma\{111\} < \gamma\{100\} < \gamma\{110\}$ [22]. Based on the principle of surface free energy minimization, the equilibrium morphology of the spinel is expected to be an octahedron, and indeed, this is the most common form in which a nanocrystalline spinel is observed [22–24].

Although 56 atoms are present within the spinel's unit cell, only 14 atoms are necessary to construct the simplest primitive cell. The factor group analysis shows that the 42 normal modes of spinel, 3 acoustic modes and 39 optical modes belong to the symmetry modes [25].

$$\Gamma (\text{AB}_2\text{O}_4) = \text{A}_{1\text{g}} (\text{R}) + \text{E}_{\text{g}} (\text{R}) + \text{F}_{1\text{g}} (\text{in}) + 3\text{F}_{2\text{g}} (\text{R}) + 2\text{A}_{2\text{u}} (\text{in}) + 2\text{E}_{\text{u}} (\text{in}) + 4\text{F}_{1\text{u}} (\text{IR}) + 2\text{F}_{2\text{u}} (\text{in})$$

The (R) and (IR) identify Raman- and infrared-active vibrational mode, respectively, and the rest of the modes marked as (in) are silent. The E_{g} and $\text{F}_{2\text{g}}$ modes are doubly and triply degenerate, respectively. The three acoustic

modes belong to a single F_{1u} mode. A common notation exists in most of the literature to distinguish between the Raman and IR modes belonging to the same representation, and will be used in the present study. The three Raman-active F_{2g} modes are labelled F_{2g} (1), F_{2g} (2), and F_{2g} (3), where F_{2g} (1) is the lowest-energy F_{2g} mode and F_{2g} (3) is the highest-energy mode of this vibrational modes. Conversely, the four IR-active F_{1u} modes are labelled ν_1 , ν_2 , ν_3 , and ν_4 in descending value of energy.

In detail, the irreducible representations that describe the normal modes of vibration associated with each atomic species in their Wyckoff positions are:

$$8a [T] : F_{1u} (\text{IR}) + F_{2g} (\text{R})$$

$$16d [M] : A_{2u} (\text{in}) + E_u (\text{in}) + F_{2u} (\text{in}) + 2F_{1u} (\text{IR})$$

$$32e [X] : A_{1g} (\text{R}) + A_{2u} (\text{in}) + E_u (\text{in}) + E_g (\text{R}) + 2F_{2g} (\text{R}) + F_{1g} (\text{in}) + F_{2u} (\text{in}) + 2F_{1u} (\text{IR})$$

The literature is inconsistent with regard to the assignment of the specific atomic motions within the spinel lattice during the Raman-active vibrations. Accordingly, it is necessary to summarize the common atomic motions assigned to the vibrations of the spinel (Table 1). The Raman band at ca. 705 cm^{-1} , A_{1g} mode, is assigned as the symmetric A^{2+} -O stretching vibration of the AO_4 unit within the spinel lattice [26–28]. The oxygen atoms move away from the tetrahedral cation along the direction of the bonds. Neither the tetrahedral nor octahedral cations are in motion during this vibration [29,30]. However, some authors demonstrated that exchanging the octahedral cation has a much greater effect upon the wavenumber of this mode than exchanging the tetrahedral cation [31], so the A_{1g} mode is mostly independent of the divalent metal occupying the tetrahedral site. This fact justifies that A_{1g} mode is viewed

as the symmetric B-O stretching vibration of BO_6 groups, and it is assigned to the A_{1g} mode in the octahedral spectroscopic symmetry [32–35]. The literature also disagrees about the assignment of atomic motions during the vibration for the F_{2g} (3) mode, which has been reported as either the antisymmetric stretching mode of the AO_4 unit [28], or as an asymmetric bending motion of the oxygen bonded to the tetrahedral cation [36]. Furthermore, by comparing the Raman shift of F_{2g} (3) in MgB_2O_4 and FeB_2O_4 spinels ($B = \text{Cr, Al, Fe}^{3+}$), a linear decreasing trend with increase of the octahedral cation radius was observed [26]. Generally speaking, this mode has been assigned to the asymmetric stretching of oxygen with respect to the tetrahedral cation [26–28], but the observed trend indicates that the F_{2g} (3) mode is related to the octahedral cation itself. Additionally, the F_{2g} (2) mode has been assigned to the A-O asymmetric stretching vibration in the tetrahedral sites [26,27], T-sites. A very good correlation was found between the peak position of the E_g mode and the tetrahedral cation radius [26]. Thus, E_g mode has been assigned to the symmetric bending motion of the oxygen atoms within the T-sites [27]. Hence, despite the movement affecting mainly the oxygen atoms, the presence of different divalent cations in the T-sites influences the E_g mode [26]. Finally, most of the authors agree that the F_{2g} (1) mode is assigned to a complete translation of AO_4 within the spinel structure [26–28,30,33].

Table 1: Overview of Raman modes for CoAl_2O_4 .

Raman Band (cm^{-1})	Symmetry Modes	Assignment	References
705	A_{1g}	Stretching symmetric AO_4 Stretching BO_6	[26–28] [32–35]
615	F_{2g} (3)	Stretching antisymmetric AO_4 Bending antisymmetric AO_4 BO_6	[26–28] [36] [26]
516	F_{2g} (2)	Stretching asymmetric AO_4	[26,27]

406	E_g	Bending symmetric AO_4	[26,27]
201	$F_{2g}(1)$	Complete Translation AO_4	[26–28,30,33]

EXPERIMENTAL

Nanodispersion procedure of α - Al_2O_3 / Co_3O_4 mixtures and thermal treatment procedure:

Compositions with 1, 5, 10, 20 and 30 wt. % of Co_3O_4 nanoparticles on α - Al_2O_3 microparticles (hereafter named as 99Al1Co, 95Al5Co, 90Al10Co, 80Al20Co and 70Al30Co, respectively) were prepared by incorporating the appropriate amounts of Co_3O_4 nanoparticles as previously described [15]. Samples were thermally treated at 1200°C with a heating rate of 3°C/min. For comparison purposes, a standard $CoAl_2O_4$ micrometric pigment (Manuel Riesgo SA, Madrid, Spain) has been used.

Characterization:

The crystalline phases were characterized by X-ray diffraction (XRD, D8, Bruker) using a Lynx Eye detector and Cu $K\alpha_{1,2}$ radiation. The X-Ray data were analysed by standard Rietveld refinement using the CHEKCELL program, assuming a face-centred cubic spinel structure with the space group $Fd3m$ (JCPDS 00-038-0814) for $CoAl_2O_4$ phase and a hexagonal corundum structure with the space group $R-3c$ (JCPDS 00-011-0661) for α - Al_2O_3 phase.

The surface composition was performed using an X-ray Photoelectron Spectrometer (XPS, K-Alpha, Thermo Scientific). It utilizes a monochromated Al $K\alpha$ (1486.6 eV) source running at a voltage of 12 KV with a pass energy of 40 eV used for high resolution region scans and 200 eV for survey scans. Finally, for charge correction a 1 point scale with the C 1s peak shifted to 284.6 eV was used.

Core-shell microparticles were observed by using a Field Emission Scanning Electronic Microscope, FESEM, Hitachi S-4700. Additionally, the nanostructure was studied by atomic force microscope, AFM, with the Witec system (Witec ALPHA 300RA) where the AFM is coupled to the confocal microscope. AFM images were taken at RT using silicon tips (with a resonant frequency of 200–300 kHz) in non-contact mode. This system allows studying the same area of an isolate microparticle in both the Raman and the AFM studies. For this purpose, the samples were deposited on a microscopy glass slide. This sample preparation does not allow us to use the intermittent contact mode, because the microparticles can move during the assay.

The Raman study was carried out with the use of a confocal micro-Raman coupled with the AFM (Witec alpha – 300R, Witec, Ulm, Germany). Raman spectra were obtained using a micro-Raman system with a 532 nm excitation laser and a 100x objective lens (NA=0.9). The incident laser power was about 5 mW on the core-shell samples and 0.5 mW on the CoAl_2O_4 pigment used as reference. The final spectrum is the result of an average of 6 spectra integrating 30 s each spectrum. Collected spectra were analyzed by using Witec Control Plus Software (Witec, Ulm, Germany).

Temperature Raman measurements between 300 K (RT) and 848 K were carried out in a temperature chamber (LinkamSystem) on compacted powders, for which argon gas was used in order to purge the sample chamber and avoid condensation in the upper lid of the window surface. This chamber is used to provide a homogeneous temperature for the whole sample under study. For each measurement point, the temperature was stabilized for 10 minutes before acquiring a spectrum for 3 min. All the Raman spectra were obtained under the

same experimental conditions, and the Raman band positions and widths were obtained by fitting them with a Lorentzian function.

RESULTS AND DISCUSSION

Micro-nanostructural characterization of shell nanostructures.

Fig. 1 (a-b) shows the FESEM micrographs of the 95Al5Co and 70Al30Co samples. FESEM micrographs illustrate the presence of crystallizations having different morphologies that cover the whole α -Al₂O₃ surface. A high proportion of these nanocrystals have a triangular shape and presents strikingly flat surfaces with low thickness and straight edges, so hereafter they will be called 2D particles. Irregular particles could also be seen, which have a hole in the middle. These particles protrude further from the alumina surface than the flat triangular ones, they are the result of the agglomeration of former nanoparticles, so we will name them 3D particles [15].

The surface roughness of the 2D and 3D structures is confirmed by AFM characterization, Fig. 1 (c-d) (For more detailed information see Supplementary Info, Fig. S1). Hence, samples with lower amounts of Co₃O₄ in their composition allow the presence of flat CoAl₂O₄ 2D particles. On the other hand, 3D rough structures are highly present in samples with a higher percentage of the former Co₃O₄ and an increase in the surface roughness of the core-shell nanostructure particles occurs with a corresponding increase of the initial cobalt oxide amount, Fig. S1 (b). In fact, the height of the CoAl₂O₄ structures increases from $\approx$ 20 nm for 99Al1Co samples to $\approx$ 100 nm for 70Al30Co samples.

Figure 1.- Micro-nanostructural analysis of core-shell nanostructured microparticles: FESEM micrographs of a) 95Al5Co and b) 70Al30Co samples; AFM topographical images of c) 95Al5Co and d) 70Al30Co samples.

Fig. 2 shows the XRD patterns of the core-shell nanostructured microparticles made with various cobalt contents. The reaction between Co_3O_4 and $\alpha\text{-Al}_2\text{O}_3$, according to the phases diagram [37] results in the formation of a CoAl_2O_4 spinel-type solid solution. The diffraction patterns are compared with that of a commercial CoAl_2O_4 used as reference. CoAl_2O_4 and Co_3O_4 have the same spinel cubic (Fd3m) crystallographic structure with slight differences in the a lattice constant: 8.1040 Å for CoAl_2O_4 and 8.0840 Å for Co_3O_4 . They therefore, have a similar peak pattern, and the positions of the XRD peaks are nearly the same, so no relevant differences between their phases could be determined by XRD. Moreover, the presence of un-reacted Co_3O_4 could not be dismissed from this technique. In any case, no evidence of metallic Co, CoO or secondary phases different from $\alpha\text{-Al}_2\text{O}_3$, Co_3O_4 or CoAl_2O_4 is found at any composition within the XRD resolution limit.

Figure 2.- XRD diffraction patterns of 100-xAlxCo series of core-shell nanostructured microparticles, CoAl₂O₄ reference, and corresponding JCPD patterns for Co₂Al₂O₄, Co₃O₄ and Al₂O₃.

Structural characterization of core-shell nanostructures.

In order to confirm the absence of a Co₃O₄ spinel at the surface of the platelets of α -Al₂O₃, an additional study was performed by XPS. The high-resolution photoelectron spectra of Co 2p for the different samples are displayed in Fig. 3. The binding energies (BE) of Co core levels of the samples are listed in Table 2. For comparison, the XPS data of raw materials (Co₃O₄ and CoAl₂O₄) are also listed in Table 2. The XPS spectra of all the samples annealed at 1200°C, as well as the references (Al₂O₃, Co₃O₄ and CoAl₂O₄), indicating that in addition to

the raw materials and contaminated carbon, sodium is detected as a contaminant specie (as shown in Supplementary Info, Fig. S2). As indicated by the XPS spectrum of α -Al₂O₃ the presence of sodium comes from the α -Al₂O₃ particles [38]. In addition, the C1s peak at 284.6 eV of contaminated carbon is used as reference.

Pure Co₃O₄ exhibits two oxidation states. On a molar basis, there are two Co³⁺ ions in octahedral symmetry and one Co²⁺ ion in tetrahedral symmetry, which are distributed on the A and B sites as [Co²⁺]_A[2Co³⁺]_BO₄. The combination of the two oxidation states results in the asymmetric shape of the Co 2p_{3/2} and 2p_{1/2} peaks [39] as observed in Fig. 3. Hence, the XPS data for Co₃O₄ spinel clearly shows the presence of a doublet of peaks, which are centred at 779.34 eV and at 780.54 eV, and a shake-up satellite peak at 784.94 eV for the Co 2p_{3/2} level. A doublet is also observed for the Co 2p_{1/2} level at 794.84 eV and 795.96 eV, and the satellite at 803.75 eV. Note too, that the energy splitting (ΔE) between the two levels, due to spin-orbit coupling, should be different for the Co²⁺ and Co³⁺ configurations: the differences in energy therefore are $\Delta E=15.10$ eV for Co³⁺ and $\Delta E=15.42$ eV for Co²⁺. These results confirm the presence of Co³⁺ and Co²⁺ in Co₃O₄ and are in good agreement with the previously reported data [40–42].

The cobalt atoms in CoAl₂O₄ are in a +2 oxidation state with tetrahedral coordination. Cobalt aluminate has also a spinel structure like cobalt oxide, but the aluminium atoms occupy the octahedral coordination. The Co 2p_{3/2} peak presents a significantly higher binding energy in cobalt aluminate than in cobalt oxide and the peak is more symmetric in cobalt aluminate because cobalt only has a single oxidation state [43]. In the case of the samples with different cobalt

content, small changes are observed in both the Co 2p_{3/2} and Co 2p_{1/2} peaks positions; they are displaced to higher binding energies as the amount of cobalt increases (Table 2). For these samples, the data give an energy splitting $\Delta E = 15.6$ eV, which is characteristic of Co²⁺ only, and no additional signatures for the Co³⁺ state are noticed. Moreover, these structures clearly show two intense satellites which are representative of tetrahedral coordinated Co²⁺ cations as they occur in CoAl₂O₄ [44]. The satellites are attributed to the transition of an electron from an occupied 3d orbital to the empty 4s orbital during the ejection of the core 2p photoelectron [45,46]. From the XPS study, the atomic percentages resulting from the quantitative analysis of the XPS spectra of the species presented in the formulated samples and in references are shown in Table 3. Reference CoAl₂O₄ presents a value for a Co:Al ratio of 1:7. This value is initially in concordance with a CoAl₂O₄ structure that ends with Aluminium atoms in octahedral positions. The aforementioned ratio is similar for samples 90Al10Co, 80Al20Co and 70Al30Co so it confirms that the core-shell is formed in these samples. In the case of 95Al5Co and 99Al1Co, the amount of Aluminium cations is slightly higher, so the surface is not completely covered by CoAl₂O₄, as observed in the FESEM study. These results confirm the coexistence of CoAl₂O₄, α -Al₂O₃ and the core-shell formation.

Figure 3.- XPS spectra of Co 2p core levels of pure Co_3O_4 and CoAl_2O_4 samples. The vertical dot lines are binding energy for the reference compounds: For the $\text{Co } 2p_{3/2}$ peak the values are 779.7 and 780.9 eV for the Co_3O_4 and 780.6 eV for the CoAl_2O_4 , whereas for the $\text{Co } 2p_{1/2}$ peak the values are 794.8 and 796.1 eV for the Co_3O_4 and 795.6 eV for the CoAl_2O_4 .

Table 2: Binding energies of Co 2p core level (eV) for 100-xAlxCo series of samples, CoAl_2O_4 and Co_3O_4 as references depending on “T_d” (tetrahedral) and “O_h” (octahedral) structures.

Sample	Co 2p _{3/2}				Co 2p _{1/2}				
	Co ²⁺ (eV)	T _d	Co ³⁺ (eV)	O _h	Sat (eV)	Co ²⁺ (eV)	O _h	Co ³⁺ (eV)	T _d
99Al1Co	780,11				784,40	795,67			801,57
95Al5Co	780,62				785,01	796,20			802,03
90Al10Co	780,68				785,07	796,26			802,06
80Al20Co	780,70				785,10	796,29			802,11

70Al30Co	780,83		785,17	796,42		802,29
CoAl₂O₄	780,56		784,92	796,17		802,01
Co₃O₄	779,34	780,55	784,94	794,44	795,96	803,75

Table 3: Element contents (%) of the samples based on XPS analysis.

Sample	At % C	At % O	At % Al	At % Co	Co:Al
Al₂O₃	8,78	47,77	43,44		
Co₃O₄	12,42	57,35		30,23	
99Al1Co	9,84	47,74	41,25	1,17	1:35
95Al5Co	7,38	49,72	38,88	4,02	1:10
90Al10Co	8,57	49,56	36,28	5,59	1:6
80Al20Co	13,18	46,94	34,49	5,39	1:6
70Al30Co	10,41	48,33	35,76	5,50	1:7
CoAl₂O₄	6,13	52,18	36,62	5,07	1:7

Fig. 4 (a) shows the Raman average spectra for the five samples and for comparison purposes the Raman spectra of α -Al₂O₃ and CoAl₂O₄ as references. Concerning α -Al₂O₃, it has been reported that α -Al₂O₃ (corundum) is based on D63d symmetry with seven Raman-active phonon modes, A_{1g} (418 and 645 cm⁻¹) and E_g (378, 429, 448, 576 and 750 cm⁻¹) [47]. CoAl₂O₄ pigment which is used as reference has a spinel structure and, considering that this spinel structure belongs to the Fd3m space group, it exhibits five Raman active modes: A_{1g} (764 cm⁻¹); F_{2g} (644, 511 and 203 cm⁻¹) and E_g (413 cm⁻¹) [26]. The main phase identified by Raman spectroscopy in the samples is the spinel CoAl₂O₄. In the 99Al1Co sample, α -Al₂O₃ is identified because its surface is not completely covered by CoAl₂O₄ nanoparticles in agreement with the XPS study. Fig. 4 (b) and Fig. 4 (c) show Raman redshift variation for the most intense Raman peaks of the CoAl₂O₄ phase, F_{2g} (1) and F_{2g} (2), as the amount of starting Co₃O₄ increases in the composition. The Raman redshift is more

pronounced for 80Al20Co and 70Al30Co samples. Moreover, a broadening of the Raman modes occurs in addition to the Raman redshift.

Figure 4.- a) Raman spectra for core-shell nanostructured microparticles of the 100-xAlxCo series, and for comparison Raman spectra of CoAl₂O₄ and Co₃O₄ as references are also included. b) Detail of the Raman shift of F_{2g} (1) mode and c) F_{2g} (2) mode. (In figures b) and c), the dashed lines serve as a visual guide).

With the aim to elucidate the origin of the redshift of Raman modes, taking into account the concentration of starting Co₃O₄, both the possible heating of the sample due to the laser irradiation and the morphology of the surface nanostructures must be considered [48–50].

In Fig. 5 (a) representative Optical Microscopy images of a core-shell nanostructured particle of each composition are shown. The characteristic platelet type of the starting α -Al₂O₃ is preserved in the core-shell particle and it

is used to locate the isolated microparticles onto the glass slide support. The microparticles are aligned with the larger face perpendicular to the Raman beam ensuring both the stability of the microparticle and its homogenous observation under Confocal Raman Microscopy. For the Raman study, the displacement of the F_{2g} (1) active Raman mode is represented by a colour code following the Raman shift colour bar (Fig. 5 (b)). A gradient in the Raman shift is observed for the different microparticles between the edges and the centre of the microparticles. Moreover, the Raman intensity for the aluminate phase is higher at the edge of the microparticles (Fig. S 3 (d)). In addition, Fig. 5 (c) represents the full width at half maximum (FWHM) of the F_{2g} (1) active Raman mode, in a colour code following the FWHM colour bar. Once again, a gradient of the FWHM is observed depending on the starting Co_3O_4 amount. Differences between centre and edge areas of the core-shell particles are also detected. Two effects could cause the origin of the higher intensity of the Raman signals for the cobalt aluminate at the particle edge: a) the presence of a higher amount of $CoAl_2O_4$ (see Fig. S 3e), which can also be related to thermal effect due to irradiation [48–50]; and b) the evanescence field generated in the edge of the platelet. Both of these factors could contribute simultaneously to the redshift. In any case, to evaluate structural changes by Raman analysis, a better approach results when Raman shifts are used instead of Raman intensities.

With the data obtained from the Fig. 5 (b) for Raman shift and from the Fig. 5 (c) for FWHM, a statistical analysis is possible by using the histograms of the different regions, where each pixel of the Raman image contains the full Raman spectrum (Fig. S 4). From the histograms, the main values of the Raman shift (Fig. 5 (d)) and FWHM (Fig. 5 (e)) for the different core-shell nanostructured

microparticles are compared as a function of the centre and edge location. The study is also performed for F_{2g} (2) active Raman mode. The histograms obtained for samples with a higher amount of cobalt show a red-shift for the Raman modes with a larger broadening as the amount of cobalt increases. In addition, the higher the Raman red-shift is, the higher FMHW is. Moreover, Raman red-shift is more pronounced at the edge region, but the FWHM is slightly higher in the centre region. This indicates that the heating process of the shell under laser irradiation provokes differences in both the centre and the edge regions that are not consistent. The CoAl_2O_4 shell is supported on $\alpha\text{-Al}_2\text{O}_3$, which is an insulating material with a wide band gap (absorption edge below 200 nm) and high reflectivity in the visible region. The alumina core of the microparticles acts as a heatsink for the heat generated at the absorbing shell. The sample with the higher amount of cobalt in its composition shows increasing roughness and grain size, which are indicative of thicker shells. The higher the volume of the cobalt aluminate shell and the lower the alumina core is, the more laser absorption occurs. However, the morphology of the particles in the shell is dissimilar for the samples with a low cobalt content, which possess higher amounts of 2D particles; meanwhile a large content of starting Co_3O_4 produce the appearance of 3D nanostructures. So the heating behaviour plays a relevant role in the determination of the structural characteristics of the core-shell nanostructured material and, as a consequence, the thermal evolution of Raman spectra must be evaluated.

Figure 5.- a) Micrographs by Confocal Optical Microscopy of core-shell nanostructure microparticles for 100-xAlxCo series. b) Raman image representation of the Raman shift of the $F_{2g}(1)$ mode of the same particles present in **a**. Bar at the bottom of the figure incorporates the colour code scale of the Raman shift. c) FWHM of the $F_{2g}(1)$ mode of the same particles present in **a** and **b**. Bar at the bottom of the figure incorporates the colour code scale of the FWHM. d) Raman shift of the $F_{2g}(1)$ mode as a function of the starting Co_3O_4 content. e) FWHM of the $F_{2g}(1)$ mode as a function of the starting Co_3O_4 content.

Thermal stability of shell Raman modes.

Taking into account the relevance of the laser power on the Raman properties of core-shell nanostructured microparticles, the Raman spectra of all samples under different **output** laser powers have been measured. The study was attempted to the most characteristic sample representatives of the 2D particles in the shell, 95AlCo5, and of the 3D nanostructures in the shell, 70Al30Co. Fig. 6 presents the evolution of the Raman shift and FWHM for F_{2g} (1) and F_{2g} (2) Raman modes for the different samples. The laser power for Raman acquisition was increased stepwise until irreversible modifications on the Raman spectra were produced, that is, the original spectrum was not recovered by reducing the **output** laser power to the minimum. The minimum excitation laser power was chosen as the one that produced a reproducible Raman signal of the spinel structure with a signal to noise ratio of >10 units of intensity (Supplementary Info Fig. S 5).

Fig. 6 shows the values of the Raman shift and FWHM versus the laser power that caused differences in evolution for each sample, in good agreement with the results in Fig. 5. Moreover, the 70Al30Co sample presents the largest red-shift and broadening at low incident laser power, >7 mW, that produces irreversible change in the structure. Meanwhile, the 95Al5Co sample shows a large range of stability, up to 40 mW: the maximum **output** laser power available in our experimental setup. In order to determine the evolution of the Raman spectra with the temperature, a study into a temperature chamber follows.

Figure 6.- Evolution of the F_{2g} (1) and F_{2g} (2) Raman mode as a function of the incident laser power for the 95Al5Co and 70Al30Co samples: a) Raman Shift and b) FWHM. (Measurements are made at Room Temperature).

Fig. 7 shows the dependence of the Raman shift and FWHM of the F_{2g} (1) and F_{2g} (2) modes versus measurement temperature. As can be observed, an increase of temperature produces both a Raman red-shifting and a FWHM broadening, the results are slightly different than the ones previously observed by varying the incident laser power, this effect is owing to the different sample preparation. In the case of the laser power study the measures were executed over isolated particles, whereas the temperature study were carried out on compacted powders, so this last measure corresponds to an agglomerated state, which presents a much intense modification of the Raman spectrum

produced by the temperature [19,51]. Both samples showed a linear behaviour with slight differences in their slopes until 500 K. For temperatures higher than 500 K, the 70Al30Co sample experiences a sudden increase of the FWHM. The thermal treatment at 500K does not change the average particle size for the CoAl_2O_4 crystallizations as an indication that the morphology of the particles remained unaltered, but it was able to remove the surface OH groups [52]. In addition, the measurements once the samples were cold can be observed in Fig. 7, the Raman Shift is completely reversible, whereas the FWHM suffers a real modification for the 70Al30Co sample. This is because the sample were not rehydrated, however after two days the measurements return to the initial values. In the case of the 90Al10Co sample, these effects are not visible because the proximity effects are not relevant for samples with less amounts of nanoparticles.

Figure 7.- Evolution of the main Raman parameter vs temperature for the 95Al5Co and 70AlCo30 samples. a) Raman Shift dependence of F_{2g} (1) and F_{2g} (2) modes as function of the temperature; b) FWHM dependence of F_{2g} (1) and F_{2g} (2) modes as function of the temperature. (The laser power on sample is about 5mW). The filled points corresponds to the measurements performed after let cold the samples.

The temperature dependence of the Raman shift in the linear regions can be adjusted by considering the following Equation 1 [53].

$$\omega = \omega_0 + \omega_0(e^{-3\alpha\gamma T} - 1) + A \left(1 + \frac{2}{\frac{\hbar\omega_0}{e^{2kT} - 1}} \right) \quad \text{Equation 1}$$

where ω_0 is the natural phonon energy at 0 K; the second term on the right-hand side is the correction due to thermal expansion where α is the thermal

expansion coefficient and γ is the thermodynamic equation of Gruneisen; the third term describes the coupling of the optical phonon to two lower energy acoustic phonons to describe the anharmonic processes occurring at high temperature where $\hbar$ is Planck's constant and K is Boltzman's constant.

The observed variation of Raman Shift of the F_{2g} (1) and F_{2g} (2) modes has been fitted to Equation 1, taking into consideration that thermal expansion should be negligible regarding the anharmonic processes [51,54–56]. The fitting is included in Fig. 7 as dashed lines for all samples and the values of the different fitting parameters are summarized in Table 4.

The temperature dependence of the FWHM can be fitted using Equation 2

$$\Gamma_T = \Gamma_0 + B \left(1 + \frac{2}{\frac{\hbar\omega_0}{e^{2kT} - 1}} \right) \quad \text{Equation 2}$$

where Γ_0 is the natural line-width broadening which is produced by effects not related to the thermal population of phonons [53]. This broadening could be produced by extrinsic sources, such as experimental artefacts introduced by the equipment, or intrinsic, due to variations of the anharmonicity of the atoms vibration in the crystal which are not dependant on the temperature, like an inhomogeneous strain [51]. The second term on the right-hand side of the equation describes the coupling of the optical phonon to two lower energy acoustic phonons [57].

Taking into account the parameters obtained from the fitting of Equation 1, the linewidths of the F_{2g} (1) and F_{2g} (2) modes are fitted to Equation 2. The fitting is shown in Fig. 7 and the obtained values of Γ_0 and B are also included in Table 4.

Table 4: Values of the fitting parameters of equation 1 and 2 for the Raman shift and the FWHM of the F_{2g} (1) and F_{2g} (2) modes as a function of the temperature.

	ω_0 (cm ⁻¹)	A (cm ⁻¹)	Γ_0 (cm ⁻¹)	B (cm ⁻¹)
95Al5Co F_{2g} (1)	205,452	-0,111	4,525	0,083
70Al30Co F_{2g} (1)	207,673	-0,260	0,051	0,298
95Al5Co F_{2g} (2)	518,712	-0,724	13,372	0,674
70Al30Co F_{2g} (2)	506,744	-0,500	15,762	1,081

The study of the F_{2g} (1) and F_{2g} (2) active Raman modes with temperature confirms the different slopes and therefore these Raman modes are temperature decoupled. The large variation of B values in Table 4 confirms the Raman modes' decoupling. This fact could be explained by the differences in the photon-phonon coupling due to their dissimilar CoAl_2O_4 crystallizations. It is well known that for bulk materials only, vibration modes at the Brillouin centre zone are allowed, whereas in the case of the nanoparticles, the interruption of phonon propagation at the nanomaterial surface produces a relaxation of this selection rule and allows vibration modes far from the Brillouin zone centre [58]. These new available vibration modes produce a strongly particle-size dependent displacement and broadening of the Raman spectrum [59]. In the 95Al5Co sample the predominated crystallizations are CoAl_2O_4 2D particles. 2D particles are isolated particles, so the phonon reflects against the boundaries of the large dimension plane of the particle diameter (Fig. 8 (a)) and remains in a confined way within the particle thickness (Fig. 8 (b)). In 2D particles the life time mechanism of phonon-coupling with the CoAl_2O_4 atom network is different depending on the space direction of phonon propagation. Differences in the mean free path for the phonons in the network results in different types and

different frequencies of vibrations of the atoms around their equilibrium position; the associated thermal energy is different in each space direction, which is translated to the decoupling of Raman modes. In the case of the 70Al30Co sample, the predominant shell crystallizations are CoAl_2O_4 3D nanostructured particles, which are the result of the sintering of several CoAl_2O_4 nanoparticles forming aggregates (Fig. 8 (c)). In this configuration phonons can be partially reflected at the particle's surface or can be transmitted to other systems as phonon bottlenecks [60]. Partially reflected phonons seem to present a slower decay, which allows a larger addition of modes out of the Brillouin zone centre than those given for the total reflected phonon in a single nanoparticle [61]. This effect produces a larger red shift and FWHM broadening for aggregated nanoparticles, which is not presented for the isolated ones. Again, the decoupling of the Raman modes is attributed to the differences in the phonon motion because of differences in crystalline structures. The mean free path of phonons is thus different for 2D and 3D nanostructures, so the anharmonicity in

phonon coupling with temperature is consistent with the differences in crystallinity of the material.

Figure 8.- Representation of phonon movement depending on the type of CoAl_2O_4 particle: a) phonon transversal to the (111) crystallographic orientation in 2D particles; b) confinement of phonons along (111) crystallographic orientation in 2D particles; and c) phonon behaviour in aggregate nanoparticles. (Phonons are represented in red and scattered phonons in green). Schematic diagram of the Raman modes: d) $F_{2g}(1)$ corresponds to a complete translation of the AO_4 units and e) $F_{2g}(1)$ mode has been assigned to the Co-O asymmetric stretching vibration in the tetrahedral coordinated sites.

As previously mentioned in Table 1, $F_{2g}(1)$ mode is assigned to a complete translation of the AO_4 units within the spinel structure (Fig. 8 (d)); whereas $F_{2g}(2)$ mode corresponds to the asymmetric stretch in AO_4 units (Fig. 8 (e)). $F_{2g}(1)$ occurrence is qualitatively higher than $F_{2g}(2)$, so it is more favorable that $F_{2g}(1)$

occurs. Additionally, Raman shift of F_{2g} (2) mode also indicates a lower energy absorption of the crystal lattice. The clear differences between both modes related to their thermal evolution indicate that the phonon transmission between adjacent particles is more likely to occur in the lower energy vibration mode, translation of AO_4 units in F_{2g} (1). The aggregation of the 3D nanoparticles area is associated with a redshift of the Raman modes, so these vibration modes are easy to heat, as occurs in the 70Al30Co sample. On the other hand, 2D particles are constrained by the alumina support as indicated by their higher bond constant force, sample 95Al5Co. The differences on the heating ratio between Raman modes F_{2g} (1) and F_{2g} (2) could be attributed to the energy difference ceded by the photons to the crystal lattice. This aspect is related to the nature of each Raman mode where the A-O asymmetric stretching in AO_4 tetrahedrons (F_{2g} (2)) is favored versus AO_4 translation (F_{2g} (1)). For this reason, F_{2g} (2) mode is more affected by heating from the incident laser power. This effect is less relevant for the 95Al5Co sample because of the reduced volume of material due to the lower thicknesses of 2D nanostructures and, in addition, to the higher laser reflectivity of α - Al_2O_3 core support.

FMHW is wider for the 70Al30Co sample as a result of their relaxed crystal structure in the aggregation state (Fig. 7 (b)). In the 95Al5Co sample, the FMHW maintains its value and the sample removes the heat efficiently. In this sense, the presence of 2D particles in the shell is more favorable - to ensure the thermal stability of core-shell particles - than the presence of 3D nanostructures. These findings open the design of new pigments with superior performance under extreme operating conditions.

CONCLUSIONS

The formation of a CoAl_2O_4 shell of isolated 2D or 3D nanoparticle aggregates onto $\alpha\text{-Al}_2\text{O}_3$ core microparticles has been demonstrated. An AFM study confirmed an increase of the roughness over $\alpha\text{-Al}_2\text{O}_3$ platelets due to the presence of CoAl_2O_4 having different morphologies. XPS characterization indicated the effective formation of a CoAl_2O_4 shell in samples having ≥ 10 wt% of Co_3O_4 . Confocal Raman microscopy revealed the structural differences between core-shell microparticles with 2D CoAl_2O_4 particles (95Al5Co) and with aggregates of 3D nanoparticles (70Al30Co). Depending on the CoAl_2O_4 nanostructure morphology, the shift and FWHM was different. In 3D the phonon confinement was correlated with a crystal structure relaxation that favoured the thermal heating. The Raman modes also decoupled with temperature for F_{2g} (1) and F_{2g} (2) modes, as consequence of their differences in energy and occurrence. The complete translation of AO_4 units in the spinel structure was limited in 2D nanostructures and the heating of the particles is accordingly limited. The thermal stability of core-shell microparticles by using the approach of 2D nanostructures opens thus an opportunity to design better pigments based on inorganic materials.

CONFLICTS OF INTEREST

The authors declare no competing financial interest.

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SUPPLEMENTARY INFO

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Figure S 1.- a) Two dimensional (2D) AFM topographical images of different samples showing the surface of the microparticle covered by nanocrystals. The black line corresponds the place where the roughness profile was calculated. b) Roughness profiles for the complete range of compositions.

The surface roughness of the 2D and 3D structures is confirmed by AFM characterization (Fig. S 1). The roughness of the core-shell nanostructured particles varies depending on the starting amount of Co_3O_4 . Hence, samples with lower amount of Co_3O_4 in composition allow the presence of isolated Co_3O_4 nanoparticles, so 2D CoAl_2O_4 particles predominate. Whereas, agglomerates are present in samples with higher percentages of Co_3O_4 and 3D particles are in the majority. The $\alpha\text{-Al}_2\text{O}_3$ sample shows the typical morphology

consisting mainly on plate type particles characteristic of this material, due to crystal growth in the ab plane.

Figure S 2.-Survey XPS spectrum of the samples.

In order to confirm the absence of a Co_3O_4 spinel at the surface of the platelets of $\alpha\text{-Al}_2\text{O}_3$, an XPS study was performed (Fig. S 2). The XPS spectra of all the samples annealed at 1200°C , as well as the references (Al_2O_3 , Co_3O_4 and CoAl_2O_4), indicating that, in addition to the raw materials and contaminated carbon, sodium was detected as a contaminant specie. As indicated by the XPS spectrum of $\alpha\text{-Al}_2\text{O}_3$, the presence of sodium comes from the $\alpha\text{-Al}_2\text{O}_3$ particles. In addition, the C1s peak at 284.6 eV of contaminant carbon is used as reference.

Figure S 3.- a) Confocal Optical Microscopy micrographs of core-shell nanostructured microparticles for 100-xAlxCo series. b) Raman image representation of the Rayleigh dispersion intensity of the particles presented in **a**. c) Raman image representation of the Raman intensity of the $F_{2g}(1)$ mode of the particles presented in **a**. d) Graphical representation of the Rayleigh dispersion intensity and the Raman intensity of the $F_{2g}(1)$ mode of the particles presented in **a**. e and f) Explicative model for higher heating of particles at the edge than in the centre.

For the Raman study, differences in the Raman Rayleigh Dispersion intensity are observed for the different microparticles between the edges and the centre

of the microparticles (Fig. S 3b). This situation is due to the morphology of α - Al_2O_3 . The edges of the platelets present more structural elements that favour light dispersion. Moreover, the Raman intensity for the aluminate phase is higher at the edge of the microparticles (Fig. S 3 (d)). This effect is due to the measure procedure, again because of the morphology of α - Al_2O_3 . On the external part, the Raman laser beam falls on more CoAl_2O_4 nanoparticles than in the case of the interior area of the core-shell (see Fig. S 3(e)). So, in the external area the intensity Raman Shift increases because the laser beam interacts with higher amounts of CoAl_2O_4 nanoparticles.

Fig. S 4.-Statistical analysis obtained from Raman study.

A statistical analysis of Raman shift and FWHM of Raman signal are represented as histograms. In this study, it was taken into account that each pixel of the Raman images contains the full Raman spectrum (Fig. S 4). From the histograms, the main values of Raman shift and FWHM for the different core-shell nanostructured microparticles were extracted as a function of the

centre and edge location. The study was performed for F_{2g} (1) and F_{2g} (2) active Raman modes.

Figure S 5.- F_{2g} (1) and F_{2g} (2) Raman active modes in spectrum for the 95Al5Co sample: a) with a laser power of 1 mW and b) with a laser power of 40mW. c) Signal to noise ratio as a function of the laser power.

Raman acquisition procedure: For the Raman study, the minimum excitation laser power was chosen as the one that produced a reproducible Raman signal of the spinel structure with a signal to noise ratio of >10 units of intensity (Fig. S 5). Thus interference, i.e. heating of the sample or modifications to the structure, was highly avoided because only the minimum laser beam power necessary for obtaining accurate results was applied.