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2D particles forming a nanostructured shell: a step forward cool NIR reflectivity for CoAl₂O₄ pigments.

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ABSTRACT

Blue CoAl₂O₄ are inorganic pigments with impressive optical effects and a high chemical stability. However, this spinel type structure has two main drawbacks: cobalt is scarce and expensive, and the dark pigment absorbs the solar spectra resulting in undesirable heating. In this work a new type of cool NIR blue pigment is attained by in-situ forming of a shell of 2D CoAl₂O₄ nanoparticles on α -Al₂O₃ microparticles. Nanodispersion of Co₃O₄ nanoparticles on the surface of α -Al₂O₃ microparticles has been carried out by means of a low energy dry mixing method and further in-situ thermal treatment at 1200°C forms a nanostructured shell. CoAl₂O₄ nanocrystals are controlled in size by the frequency size of the previously dispersed Co₃O₄ nanoparticles. 2D particles form to fill the distance between Co₃O₄ nanoparticles on the alumina surface. The new shell structure makes it possible to obtain a high efficient NIR pigment with a solar reflectance SR>70% and a large cobalt content reduction. A sample containing only 10 wt. % of cobalt shows similar chromatic coordinates to standard bulk pigments, which means a significant saving of raw materials.

INTRODUCTION

The use of pigments is highly prevalent in today's society. The application fields cover different areas such as textiles, printing, polymers, interior and exterior coatings, etc. Inorganic pigments enable high durability and colour stability under extreme conditions such as UV radiation, temperature or chemical attack. Among others, spinel-type oxides are an important family of compounds with the general formula AB₂O₄, where A and B stand for two different cations of comparable ionic sizes. The crystal lattice of the normal spinel consists of a cubic close packing of oxygen atoms and A²⁺ and B³⁺ cations occupy two different crystallographic sites, tetrahedral and octahedral,

respectively [1]. Owing to their physicochemical properties and that they are a class of chemically and thermally stable materials, they are suitable for a wide range of applications of extensive use such as ceramics materials [2], magnetics [3], electronics [4], and catalysis [5].

Among spinel materials, cobalt aluminate, CoAl_2O_4 , is widely used in several fields as a pigment because of its intense blue colour [6], which is commonly known as Thenard's blue. Today's pigments face new challenges owing to higher yields, sustainability and new functionalities. One such technology is the use of specialty infrared reflective pigments which are applied to impart colour to an object and to reflect the invisible heat from the object, in order to minimize heat build-up when the objects are exposed to solar radiation [7]. Ultimately the reflection of solar energy lowers the heat build-up resulting in a reduction on the load of the cooling system and therefore a cost saving [8]. There are currently a number of cool materials commercially available for buildings and other surfaces in the urban environment. Most of these materials are white or light-coloured [9]. However, there is a need for cool non-white products because in many cases the aesthetics of darker colours is preferred. Our cobalt aluminate is a dark pigment and has high near infrared (NIR) reflectance. Hence, by using this material we can keep the coated surface of roofs cool while enhancing the aesthetics of the built environment.

The use of nanoparticles improves the functionality of the materials; for instance, nanopigments enhance mechanical properties such as scratch, abrasion resistance, hardness and strain-to-failure [10] or allow the use of mild temperatures in synthesis [11]. However, smaller particles as nanoparticles have higher specific surface and reactivity that could potentially cause toxic health effects through human exposure [6,12]. Therefore, the increase of the industrial use of cobalt nanoparticles has led to many recent in vitro toxicological studies [13]. These studies have shown that cobalt is genotoxic [14], induces oxidative stress [15], apoptosis [16], and is a hypoxia-simulating agent [17]. Moreover, cobalt particular limitation is related to scarcity and

cost. In this sense, the solution of the harmful collateral effect of nanotechnology could be addressed by using nanostructured microparticles.

In recent years, the study of core-shell composite particles has attracted increasing attention because of their potential applications, especially in the biomedical [18] and electronics fields [19]. The resulting composite particles often combine large particles with nanoparticles; for example, silica and metal nanoparticles have been applied widely for the development of various core-shell materials [20]. Complex pigments obtained through chemical routes consist of a core rutile TiO_2 and a spinel CoAl_2O_4 shell that exhibit good colour properties with enhanced NIR reflectance [21] but still have a limited Al^{3+} to Co^{2+} ratio of 3 as standard spinel [22]. Several techniques have been demonstrated for depositing metal nanoparticles onto inorganic cores, including seed methods [23], thermal evaporation techniques [24], self-assembly methods [25], electroless plating [26], and sol-gel methods [27]. However, these approaches are really expensive and almost always result in non-uniform or low particle densities in the shell area.

Previous studies have shown a methodology to effectively disperse Co_3O_4 nanoparticles onto $\alpha\text{-Al}_2\text{O}_3$ microparticles by using a dry dispersion process [28,29]. Nanoparticle dispersion and anchoring effects occur at room temperature through an electrochemical reaction between these materials due to the high initial reactivity of the Co_3O_4 [30]. This procedure to de-agglomerate nanoparticles has also been applied previously in different systems [28,31,32], producing novel properties at the interfaces. The aim of this work is to design a safety method to obtain a core-shell structure, where the shell is nanostructured. In this study, further thermal treatment of dispersed Co_3O_4 nanoparticles on $\alpha\text{-Al}_2\text{O}_3$ microparticles provides 2D nanoparticles of CoAl_2O_4 spinel type. So we prepared core-shell particles by assembling a layer of 2D CoAl_2O_4 nanoparticles using a facile and massive method. The core-shell structure reduces notably the amount of required cobalt and minimizes its potential toxicity effects. Moreover, solar reflectivity is enhanced by achieving values higher than 70% in the NIR

range with the same chromatic coordinated as standard bulk pigments. These materials represent a step forward towards designing an efficient and sustainable pigment that could act as cool pigment under solar radiation applications.

EXPERIMENTAL PROCEDURE

Nanodispersion procedure of α -Al₂O₃/Co₃O₄ mixtures and thermal treatment procedure:

Compositions with 1, 5, 10, 20 and 30 wt. % of Co₃O₄ nanoparticles on α -Al₂O₃ microparticles (hereafter named as 99Al1Co, 95Al5Co, 90Al10Co, 80Al20Co and 70Al30Co, respectively) were prepared by incorporating the appropriate amounts of Co₃O₄ nanoparticles by a previously described dry solid state method. The dry dispersion process consisted of shaking the materials' mixture using an acoustic-type mixer. The raw materials used in this study were 20 nm nanoparticles of cobalt oxide (Co₃O₄, Aldrich, Wadena, MN, USA) having high purity (>99.9%), forming large agglomerates of >5 μ m in average diameter, and ~6.0 μ m size microparticles of aluminium oxide (α -Al₂O₃, Vicar, S.A. Manises, Spain) having a purity of >99.5%. The powders were dried at 80°C for 24 h before dry mixing. It was carried out the thermal treatments at different temperatures in the 850°C to 1300°C range with a heating rate of 3°C/min.

Characterization:

Thermal behaviour of materials was studied by means of differential thermal (TDA) and thermogravimetric (TG) analysis using a Thermo-Analyzer Netzch STA 409 with a temperature controller Netzch TASC 414/2. It was carried out in the range 20-1300°C with the same heating rate as in the synthesis process (3°C/min).

UV-Vis diffuse reflectance spectra of the samples were recorded using a Perkin Elmer Lambda 650 UV-Vis spectrophotometer with an integrated sphere attachment. The Kubelka-Munk function was used to transform the results from diffuse reflectance to absorbance. The points were measured every 2 nm each second. The solar reflectance (SR) in the wavelength range from 700 to 2500 nm was calculated according to ASTM standard number E891-87, where the reflectivity spectrum is

integrated with the considered spectra of solar irradiance AM1GH in accordance with the formula:

$$SR = \frac{\int_{700}^{2500} r_{\lambda} i_{\lambda} d\lambda}{\int_{700}^{2500} i_{\lambda} d\lambda}$$

where r_{λ} is the experimentally obtained spectral reflectance (W m^{-2}) and i_{λ} is the solar spectral irradiance ($\text{W m}^{-2} \text{ nm}^{-1}$).

In order to assure the optical properties of the prepared pigments, the CIE- $L^*a^*b^*$ colour measurements were also performed using a spectrophotometer (Konica Minolta CM 2600d/2500d) in the 300-800 nm range. This method used the reflectance data in the visible region to obtain the three relevant parameters, $L^*a^*b^*$, indicating the brightness, red-green, and yellow-blue hue intensities, respectively. The parameter C^* (chroma) represents the saturation of the colour and is defined as $C^* = \sqrt{(a^*)^2 + (b^*)^2}$. For comparison purposes a commercial blue pigment of CoAl_2O_4 composition (Manuel Riesgo) has been evaluated and used as reference.

For the study of the morphology and the corrected dispersion of the nanoparticles over the microparticles, the new micro-nano composite was observed by using a Field Emission Scanning Electronic Microscope, FESEM, S-4700 from Hitachi. In addition, the nanostructure was studied by atomic force microscope, AFM, in non-contact mode with a WITec 300 microscope.

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 ($\text{NA} = 0.9$). The incident laser power was 5 mW for the samples and 0.5 mW for the CoAl_2O_4 pigment used as reference. The system allows studying of the same area of the sample by selecting the adequate objective of the microscope. Samples were deposited on a microscopy glass slice. Collected spectra were analyzed by using Witec Control Plus Software (Witec, Ulm, Germany).

RESULTS AND DISCUSSION

Morphology of the nanodispersed α -Al₂O₃/Co₃O₄ mixtures

The morphology of a mixture of α -Al₂O₃ with 5 wt. % of Co₃O₄ nanoparticles (95Al5Co sample) is shown in Figure 1. Figure 1a shows the α -Al₂O₃ morphology consisting mainly of plate type particles characteristic of this material, due to crystal growth in the ab plane. The Co₃O₄ nanoparticles are intuited on the α -Al₂O₃ microparticles surface. Figure 1b shows dispersed Co₃O₄ nanoparticles having diameters of 10-30 nm. The nanoparticles form agglomerates of several tens of nanometers as the Co₃O₄ amount increases, as shown in Figure 1c (90Al10Co sample).

The micrographs show that former Co₃O₄ agglomerates disappear and individual nanoparticles are adhered to the α -Al₂O₃ surface (Figure 1b). For Co₃O₄ contents <10 wt. % nanoparticles are completely dispersed over the surface of the α -Al₂O₃ particles, whereas for higher Co₃O₄ contents nanoparticle agglomerates started to appear (Figure 1c). This means that there is a “saturation amount” of Co₃O₄ nanoparticles. In all of the samples there is an alumina surface that is free of nanoparticles. The higher the amount of Co₃O₄ the lower the alumina surface is.

Thermal evolution of mixtures

In order to evaluate the thermal evolution of the different samples, DTA/Tg curves of the mixtures and of Co₃O₄ as a raw material are shown in Figure 2. The temperature range of 600-1300°C is selected to show relevant changes. In a first approach, an endothermic reaction with a mass loss of the cobalt (II) (III) oxide occurs at ca. 930°C. The mass losses correspond to the oxygen release to produce CoO [33]. By comparison of the mass losses in the mixture with the pure Co₃O₄, higher temperatures are required to complete the mass loss that indicates a plausible stabilization of the nanoparticles. However, the differences in scale mass losses could mask this effect. In a second approach, the DTA shows a more relevant change with the cobalt amount (details shown in Figure 2g). Both the peak shape and the temperatures at which the reaction takes place depend on the Co₃O₄ amount. Pure Co₃O₄ (Figure 2f) shows an asymmetric endothermic peak (peak marked as 4') with an onset at 900°C and extents

up to 955°C. Peak asymmetry is attributed to the high agglomeration state of pure nanoparticles. In these agglomerates, external nanoparticles are preferentially exposed to both atmosphere and temperature; meanwhile the oxygen diffusion is more difficult through the nanoparticles into the agglomerate. Hence, inner cobalt nanoparticles into the agglomerate require a longer time and a higher temperature to complete the reduction process than the external ones. As the amount of Co_3O_4 decreases, the endothermic peak content occurs at a lower temperature (peak marked as 4) and the process takes place in a short range of temperatures with a higher onset temperature. This effect is in agreement with the large agglomerate size reduction due the attrition effect of the $\alpha\text{-Al}_2\text{O}_3$ microparticles during the dry dispersion. Down to 10 wt. % of Co_3O_4 the endothermic peak splits into two peaks (marked as 1 and 2) that are related to the appearance of cobalt nanoparticles in contact with the alumina surface and small agglomerates.

Co_3O_4 nanoparticles anchored on $\alpha\text{-Al}_2\text{O}_3$ microparticles are partially reduced due to the electrochemical reaction during the dry dispersion process, as was previously described [30]. Moreover, the Co-O bond strength slightly varies with the amount of nanoparticles in an agglomerate [29] and thereby the lower the number of nanoparticles the higher the temperature to produce the reduction. Peaks 1 and 2 are also present in the DTA/Tg curves of 80Al20Co and 70Al30Co samples, but the high presence of Co_3O_4 agglomerates limited their resolution.

At higher temperatures than the exothermic peak region, a trend of the DTA base line to increase as an indication of the mass transport processes. There is an inflexion at $\sim 1017^\circ\text{C}$ for mixture samples (marked as 3) that can be attributed to the spinel CoAl_2O_4 formation according to the reaction:

As the reaction occurs in solid state regime, it is expected that the active Co-cations enter into the more stable alumina crystal lattice and the diffusion mechanism controls this reaction [34]. It is worth mentioning that the lower the amount of nanoparticles the

higher the energy increase in terms of μV after the inflexion point marked as 3. This fact could be associated with low site presence of former cobalt nanoparticles at the surface and indicates a large requirement of heat absorption for low cobalt content. A further inflexion point is observable at ca. 1060°C that is present in all the samples including the pure Co_3O_4 . At this temperature coarsening of cobalt nanoparticles is expected as the mass transport mechanism responsible for increasing of the ATD base line in this system. This indicates that in addition to the spinel reaction at $\sim 1017^\circ\text{C}$, there is a residual amount of CoO during the non-isothermal treatment.

To sum up, according to the thermal measurements performed in the mixtures, two different behaviours took place due to the elimination of oxygen from the Co_3O_4 reduction: lower temperature (914°C) for isolated Co_3O_4 nanoparticles on $\alpha\text{-Al}_2\text{O}_3$ microparticles and higher temperatures (927°C) from Co_3O_4 agglomerates. These differences on the Co_3O_4 distribution will cause differences in the spinel reaction pathway.

In order to evaluate the effect of the iso-thermal treatment on the phases evolution, the mixture of $\alpha\text{-Al}_2\text{O}_3$ with 10 wt. % of Co_3O_4 were thermally treated at 850, 1000, 1100, 1200 and 1300°C for 1 h. The identification of crystalline phases by XRD is shown in Figure 3a. The XRD diffractograms are normalized to the (104) crystallographic plane of $\alpha\text{-Al}_2\text{O}_3$ at $2\theta \approx 35^\circ$. No evidence of metallic Co , CoO or any additional phases different to $\alpha\text{-Al}_2\text{O}_3$, Co_3O_4 or CoAl_2O_4 are found at any temperature within the XRD resolution limit. The expected reaction between Co_3O_4 and $\alpha\text{-Al}_2\text{O}_3$ is the formation of a CoAl_2O_4 spinel-type solid solution. However this phase is isostructural with Co_3O_4 , both of them present a space group $\text{Fd}3\text{m}$ symmetry [22], and therefore X-ray diffraction patterns fail to determine whether the CoAl_2O_4 spinel forms.

The area of the (104) peak corresponding to the $\alpha\text{-Al}_2\text{O}_3$ phase is then compared with the area of the signal at $2\theta \approx 37^\circ$ corresponding to the (311) peak of the spinel phase (Figure 3b). The ratio between the areas of both peaks decreases significantly when the temperature increases, as an indication of the spinel reaction is favoured at a

higher temperature. For every three moles of CoAl_2O_4 formed, one mole of Co_3O_4 is reduced, so the spinel amount should increase due to the reaction stoichiometry and this fact is verified by XRD. For all temperatures, the presence of alumina in the sample is joined to the presence of spinel phase. This experimental evidence is in concordance with the reaction processes described by DTA points and is related to the possibility of a core-shell formation.

Optical response of synthesized pigments

Figure 4a shows ultraviolet-visible spectra for pigments having 90Al10Co synthesized at different temperatures (changes in colour for 90Al10Co sample as a function of the iso-thermal treatment temperature are appreciable in Figure 4b). The pigments synthesized at temperatures $<1000^\circ\text{C}$ show a green colour and pigments synthesized $>1000^\circ\text{C}$ show blue. The blue colour is described to be due to Co^{2+} in tetrahedral sites, while the green colour is observed for Co^{3+} in octahedral coordination. In order to determine the temperature at which the cobalt aluminate formation takes place the presence of the species Co^{2+} and Co^{3+} allow for the phase development.

The products treated at lower temperatures ($T \leq 1000^\circ\text{C}$) progress with the increase of temperature. The sample treated at 850°C is dark green and it has two wide bands, one at 800-580 nm and the other at 580-250 nm. Both bands are related to charge transfer (CT) process [35]. The band at 800-580 nm is a ligand to metal charge transfer (LMCT) band, which is assigned to the electron transference from O^{2-} to Co^{3+} in octahedral position. The band at higher energy (580-250 nm) is another ligand to metal charge transfer (LMCT) band related to the electron transference from O^{2-} to Co^{2+} in tetrahedral position. The spectrum of sample at 850°C is similar to the Co_3O_4 one [36] and no reaction took place, in agreement with DTA/Tg analysis. The pigment treated at 1000°C presents more Co^{2+} because of the reduction reaction at 914°C . The wide band at 800-580 nm splits into several bands because of the d-d transitions of Co^{2+} in tetrahedral position. In addition, a wide band appears nearly 720 nm related to the Co^{3+} in octahedral sites.

The spectra of the samples iso-thermally treated at temperatures of $\geq 1100^\circ\text{C}$ are similar between them. In addition they are similar to the CoAl_2O_4 spectrum [37]. These spectra are composed of bands corresponding to the allowed transitions of Co^{2+} electrons at $3d^7$ orbitals in a tetrahedral coordination, ${}^4\text{A}_2 (\text{F}) \rightarrow {}^4\text{T}_1 (\text{P})$. These transitions correspond to the bands at 554, 584 and 622 nm [35]. The blue colour is due to the absorption of light at this range. The higher the synthesis temperature, the stronger the blue colour the sample presents. It suggests that a higher amount of Co^{2+} at tetrahedral positions is observed when temperature increases and so more spinel is formed with temperature [38]. This is in agreement with XRD results and confirms the coexistence of CoAl_2O_4 and $\alpha\text{-Al}_2\text{O}_3$ but the core-shell formation required further proofs. Two bands at 480 and 408 nm are also observed which are assigned to the forbidden spin transitions d-d of Co^{2+} in tetrahedral positions ${}^4\text{A}_2 (\text{F}) \rightarrow {}^2\text{T} (\text{G})$ [22,35,37]. For this reason, the intensities of both bands are low in comparison with the rest of bands.

UV-Vis spectroscopy determines the optimum temperature for the synthesis of the CoAl_2O_4 spinel. The pigment treated at 1100°C for 1 hour shows similar behaviour to a reference stoichiometric pigment (not included in the graph for the sake of clarity), although the band associated with metal charge transfer (LMCT) related to the electron transference from O^{2-} to Co^{2+} in tetrahedral position is still appreciated. In addition, the pigment treated at 1300°C for 1 hour shows similar behaviour to the pigment treated at 1200°C . So taking into account these results, 1200°C seems to be the more suitable temperature for the synthesis of CoAl_2O_4 spinel by a solid-state reaction.

In Figure 4c, it is compared the CIE- $L^*a^*b^*$ colorimetric study of 90Al10Co pigments treated at different temperatures and a commercial CoAl_2O_4 blue pigment used as reference, in the centre of the colorimetric. Two trends are clearly differentiated by colour: samples treated at 850 and 1000°C whose colour coordinates tend to green and yellow, and present more darkness; whereas, the colour coordinates of the samples thermally treated at $\geq 1100^\circ\text{C}$ are quite close to the reference spinel. In fact,

1200°C and 1300°C seem to be the most similar samples although only less than 23% of the cobalt amount necessary to form the cobalt aluminate phase (the stoichiometric cobalt aluminate required an equivalent content of 44 wt. % of Co_3O_4) has been used. According to the UV-Vis spectroscopy results, it was chosen 1200°C as optimum temperature for the synthesis of this compound. Owing to the possibility to transfer this technical to the industry, 100°C of difference involves a considerably energy saving. Moreover, the blue colour is an indication that the spinel formation occurs at the surface of the alumina microparticles and thereby a core-shell is developed. The chroma value C^* that represents the richness of the colour hue is very high for the 90Al10Co pigment, with a value of 44.3 that does not change remarkable respect to the reference pigment with a value of 47.7. The chroma value is considerably high if compared with other chroma values obtained in CoAl_2O_4 nanopigments 35.2 [39] or even with the large values of recent new blue nanopigments such as $\text{Yin}_{0.9}\text{Mn}_{0.1}\text{O}_3\text{-ZnO}$ that reaches a chroma value of 42.2 [40]. An evolution of CIE-L*a*b* coordinates is observed in the colorimetric diagram of pigments treated at 1200°C for 1 hour with cobalt amounts, Figure 4d. In spite of the higher cobalt content the 90Al10Co pigment is still the most similar to the reference pigment. The samples synthesized with <10 wt. % of cobalt nanoparticles increase b^* coordinate and reduce a^* coordinate in addition to large increases of whitening, as the cobalt amount decreases. The reduction of cobalt amount accounts for a reduced reaction with alumina and thus the alumina contributed to the colour response. Nevertheless, samples synthesized with >10 wt. % of nanoparticles increase the b^* coordinate and show a tendency towards higher darkness as the cobalt amount increases. The presence of nanoparticle agglomerates in the precursor seems to limit the development of the cobalt aluminate.

To sum up, a complete formation of the cobalt aluminate has been stated for pigment with <23 wt. % content of cobalt oxide than the stoichiometric counterpart. The colorimetric analysis showed that a highly rich blue chroma is achieved for this pigment that accounts for a core-shell formation in which the cobalt aluminate forms the shell.

The pigment is obtained from the thermal treatment of dispersed Co_3O_4 nanoparticles on the surface of alumina microparticles. As the precursor showed alumina surface free of cobalt nanoparticles, the formation of a cobalt aluminate shell requires high mobility of cobalt cations along the alumina surface. Hence an in-depth study on the microstructure of the new pigment is required.

Shell structure and microstructure

In order to determine the structure of the spinel phase a Confocal Raman Microscopy analysis is attempted. Figure 5a shows an Optical Microscopy micrograph of a single particle of 90Al10Co composition treated at 1200°C for 1 hour. The same observed area serves to generate a Raman image of the surface (Figure 5b).

Figure 5c shows the Raman spectrum which corresponds to the 90Al10Co pigment and for comparison purposes the Raman spectra of $\alpha\text{-Al}_2\text{O}_3$ and CoAl_2O_4 particles as references. Concerning $\alpha\text{-Al}_2\text{O}_3$, it has been reported that $\alpha\text{-Al}_2\text{O}_3$ (corundum) is based on D_{3d}^6 symmetry with seven Raman-active phonon modes, $2A_{1g} + 5E_g$, at 378, 418, 429, 448, 576, 645, and 750 cm^{-1} [41]. CoAl_2O_4 pigment used as reference has a spinel structure and, considering that spinel structure belongs to the $Fd3m (O_h^7)$ 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}) [42]. The main phase identified by Raman in the 90Al10Co sample is the spinel CoAl_2O_4 (signalled in blue colour). This sample also exhibits the five expected Raman active modes which correspond to CoAl_2O_4 in this spectral range: A_{1g} (775 cm^{-1}); F_{2g} (646, 513 and 204 cm^{-1}) and E_g (417 cm^{-1}). All modes exhibit a blue-shift compared to the reference pigment, this fact indicates that the constant force is higher and could attribute to crystal stress in the spinel particles. This effect cannot be attributed to differences in heating by the incident laser because for the 90Al10Co sample the laser power was 5 mW, whereas for the pigment used as reference the laser power was 0.5 mW. The difference in laser power is due to the efficiency in power dissipation of heat from the sample 90Al10Co, possibly through the core-shell structure. Moreover, a higher laser power could heat the sample more and as a result a

red-shift would occur, which has not been the case. There is even a small controversy between the coefficients of thermal expansion, CTE. In the literature data, the CTE of alumina is slightly higher ($9.09 \times 10^{-6} \text{ K}^{-1}$) [43], than the CTE of CoAl_2O_4 ($8.7 \times 10^{-6} \text{ K}^{-1}$) [44]. This difference could contribute to the compression stress of the supported 2D spinel particles as indicated by the Raman blue-shift.

The Raman intensity of the spinel is higher at the edges of the particles. This fact could be associated to the evanescent field which was concentrated there. The Raman intensity of the $\alpha\text{-Al}_2\text{O}_3$ phase is rather lower than the Raman intensity of the spinel phase so the presence of alumina is difficult to determine. It is worth remarking that the laser spot has ca. 500 nm in diameter and 700 nm in depth. As the average thickness of pigment particles is 1 μm the laser spot should cover the alumina core. However the presence of a cobalt aluminate shell absorbs effectively the 534 nm laser as stated from the absorbance UV-Vis spectra.

Figure 6a shows the FESEM micrographs of the 90Al10Co sample which was treated at 1200°C. FESEM micrographs illustrate the presence of 2D surface crystallizations having different morphologies that cover the whole $\alpha\text{-Al}_2\text{O}_3$ surface (Figure 6b). A high proportion of these nanocrystals have a triangular shape and present strikingly flat surfaces with low thickness and straight edges, as shown in Figure 6c. Additionally, Figure 6d reveals other features of 2D particles, which present a triangular hole in the middle. Several irregular particles could also be seen in which the triangular shaped crystallizations are restricted and resemble an earlier stage of the sintering between former cobalt oxide nanoparticles. These irregular particles are more protruded from the alumina surface than the triangular ones. The surface has particles with different heights and spinel crystallization seems to extend the covering beyond the sites in which former Co_3O_4 nanoparticles are initially anchored. However the FESEM micrographs fail in resolution to determine if the alumina surface is completely covered by the cobalt aluminate particles.

The surface of the particles is studied by Atomic Force Microscopy, Figure 7. The first observation is that the whole surface of the microparticle is covered by nanocrystals (Figure 7a). Specifically, well-defined triangular particles and irregular small nanoparticles form a continuous shell over the $\alpha\text{-Al}_2\text{O}_3$ surface. The roughness profiles from AFM of selected regions (Figure 7b-d) confirms that the highly protruded regions are <50nm, and correspond to former small agglomerates of Co_3O_4 . The triangular shaped particles present a flat surface with a height down the 15 nm (see point 2 and 3 in Figure 7c). Initial Co_3O_4 presents a particle size ranging between 10-30 nm and this value is in accordance with the height of the AFM profile in which protruded regions lie down the two former nanoparticle heights. The triangular shaped flat particle implies a surface diffusion of cobalt cations to react with the other layer of alumina. The effective formation of a shell is based on a correct dispersion of Co_3O_4 nanoparticles and the 10 wt. % is the optimal amount to obtain a corrected yield for the formation of a CoAl_2O_4 shell in $\alpha\text{-Al}_2\text{O}_3$ microparticles.

Schematic diagram of the Shell Formation Mechanism

In order to propose a mechanism about the formation of a 2D shell, a schematic model has been developed and represented in Figure 8. The results of the previous observations have been taken into account and are depicted on the scheme.

The dry dispersion procedure provides Co_3O_4 nanoparticles anchored to the $\alpha\text{-Al}_2\text{O}_3$ surfaces. Isolated nanoparticles and small agglomerates are observed in conjunction with uncovered alumina spaces for the optimum amount of 10 wt. % of Co_3O_4 . The small agglomerates consist of a few nanoparticles that do not protrude in excess from the alumina surface. On the other hand, FESEM images show that there is a “saturation amount” of Co_3O_4 ; so Co_3O_4 nanoparticles can be effectively dispersed over $\alpha\text{-Al}_2\text{O}_3$ microparticles before a large presence of agglomerates. Definitely, two different scenarios of dispersion exist: well dispersed isolated nanoparticles and agglomerates with different nanoparticle content. The larger the amount of cobalt nanoparticles is, the larger the number of agglomerates there are and as a

consequence their size increases. Regarding the DTA/Tg analysis, it was stated that the well-dispersed nanoparticles produce higher heat during the spinel formation than the agglomerated nanoparticles. This amount of heat is considerably higher if it is taken into account that the amount of well-dispersed nanoparticles is limited by the available alumina surface sites. In addition, the agglomerates show a trend to stabilize the CoO and therefore there is a competition between the spinel formation and the sintering of CoO nanoparticles. Consequently two different crystallization pathways could occur during the thermal treatment. It has been reported that the spinel crystal prefers to form an octahedron with eight (111) surfaces, as shown in Figure 8a, because of the lower energy at these planes [45]. Depending on the octahedron orientation the structure seems to be different. For instance, the triangle shaped particles correspond to a 111-oriented octahedron [46,47], Figure 8b. The formation of 2D particles as flat shaped triangles corresponds to the isolated nanoparticles on the alumina surface. The spinel crystallization requires the mass transportation by surface diffusion of cobalt cations according to their epitaxial relationship with the substrate. This mechanism is possible because to form spinels from oxides a non-equilibrium interdiffusion is always involved during the reactions [48]. In this case, the in-diffusion of the shell material is faster than the out-diffusion of the core material, so the particle growth following the alumina surface in one of the facile spinel orientations.

Appearances of void between different triangular shaped particles during growing (Figure 8c) represent evidence of such a surface diffusion to form 2D particles on the alumina surface. The reason is that cobalt nanoparticle agglomerates allow the mass transport to form sintering necks and then to coalesce in larger particles. It is worth noting that surface diffusion to form the sintering neck does not imply crystal reorientation and therefore the large particles possess different crystal orientations. Afterwards, the spinel reaction takes place and the existence of different crystal orientations with lower surface energy than the former nanoparticles limits the spinel reaction mechanism. Holes inside these particles are an indication that the spinel

formation slows the sintering process between the cobalt nanoparticles. The appearance of agglomerates is thus a limitation of the formation of planar 2D particles. Whatever the mechanism of crystallization of CoAl_2O_4 from Co_3O_4 nanoparticles at the surface of $\alpha\text{-Al}_2\text{O}_3$ microparticles was, a core-shell is formed. These core-shell particles are composed by a core of $\alpha\text{-Al}_2\text{O}_3$ and a shell of CoAl_2O_4 nanocrystallizations.

Effective Solar Reflectivity of 2D shell pigments.

Cool pigments is one of the most challenging topics to counteract urban heat island [49,50]. The core-shell concept having 2D particles here developed produces a high chroma value of the blue colour in the visible region of the electromagnetic spectrum. However, 52% of the irradiance of the solar energy lies in the near infrared region (700-2500 nm) [51]. On other hand, NIR irradiance penetration is deeper than visible irradiance, so the effectiveness of the shell in visible response could be combined with the good NIR reflection of the alumina core.

Figure 9 shows the NIR response of 2D shell pigments with different cobalt content. Both the R^* (Reflectance) and the SR (Solar Reflectance) enhanced >40% and >10%, respectively, in the 90Al10Co pigment by comparison with the commercial. The obtained values for $R^*=77\%$ are quite large when compared with current literature data in cool NIR pigment for CoAl_2O_4 as 47% [39] or new compositions that reach 67% [40]. It is worth mentioning that the commercial pigment that we use as standard possesses a large R^* of 55%, in addition to their colour yield, that corresponds to an optimized industrial pigment. In terms of SR , the values of the 2D shell composition are 72%, again superior to the commercial pigment. The advantage of the core-shell pigment is related to the effectiveness of the 2D particles that reach high crystallinity due to their surface growth mechanism. The presence of protruded spinel nanocrystals originated in agglomerates of formed Co_3O_4 limited in that sense the effectiveness and a more refined procedure to maximize the planar particle represents a challenge for core-shell pigments.

To sum up, we have obtained a CoAl_2O_4 blue pigment, using less amount of cobalt oxide (10 wt. %) than the amount required to form the stoichiometric cobalt aluminate (44 wt. %). This is due to the formation of a core-shell structure consisting of a 2D CoAl_2O_4 nanoparticles shell over a $\alpha\text{-Al}_2\text{O}_3$ core. The mentioned structure allows improving the yield of the colour generated by the pigment despite the cobalt oxide decrease. In addition, the results revealed that the formation of the composite $\text{Al}_2\text{O}_3\text{-CoAl}_2\text{O}_4$ not only reduced the cost but also increased near-infrared solar reflectance ($R^* > 77\%$) with respect to the conventional pigments ($R^* > 47\text{-}67\%$). These facts express the potential of the CoAl_2O_4 core-shell pigment to be employed in cool coatings and opens new study fields.

CONCLUSIONS

An effective dry dispersion method was used to obtain Co_3O_4 nanoparticles dispersed over $\alpha\text{-Al}_2\text{O}_3$ microparticles. Co_3O_4 isolated nanoparticles and agglomerates are deposited on the $\alpha\text{-Al}_2\text{O}_3$ microparticles surface. The different dispositions of Co_3O_4 promote variations at its reduction temperature because of the different ways oxygen diffuses. A correct dispersion was observed up to 10 wt. % of Co_3O_4 nanoparticles and 1200°C seems to be the more suitable temperature for the synthesis of CoAl_2O_4 spinel by a solid-state reaction. Hence, core-shell particles of $\text{Al}_2\text{O}_3\text{-CoAl}_2\text{O}_4$ are achieved.

Two mechanisms of 2D CoAl_2O_4 crystallization over an $\alpha\text{-Al}_2\text{O}_3$ surface are observed: arrangement of Co_3O_4 agglomerated nanoparticles on the surface of $\alpha\text{-Al}_2\text{O}_3$, and diffusion mechanism of isolated nanoparticles on the surface of $\alpha\text{-Al}_2\text{O}_3$. The correct formation of the core shell was demonstrated by Raman Spectroscopy and by colorimetric and UV-Vis spectroscopy studies. The colorimetric study shows that the new core-shell pigment presents a high chroma blue value which is similar to a reference CoAl_2O_4 pigment. Finally, the effective solar reflectivity of the new core-shell pigment is superior to the commercial one due to the high crystallinity of the 2D CoAl_2O_4 because of its surface growth mechanism.

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FIGURE CAPTIONS

Figure 1. FESEM micrographs of Co_3O_4 nanoparticles dispersed on $\alpha\text{-Al}_2\text{O}_3$ microparticles. a) and b) 95Al5Co and c) 90Al10Co.

Figure 2. DTA/Tg curves up to 1200°C at a 3°C/min rate of the precursor mixtures: a) 99Al1Co, b) 95Al5Co, c) 90Al10Co, d) 80Al20Co, e) 70Al30Co and f) reference Co_3O_4 . (g) Detail of the endothermic signal in DTA curve for samples with different Co_3O_4 amounts. The numbers next to the peaks represent different endothermic and/or exothermic processes which occurred during the thermal analysis of the mixtures.

Figure 3. a) XRD patterns corresponding to the mixture of 90Al10Co iso-thermally treated at different temperatures (850-1300°C). b) Ratio between the (104) peak area corresponding to $\alpha\text{-Al}_2\text{O}_3$ phase and the (311) peak area corresponding to the spinel phase.

Figure 4. a) UV-Visible spectra of 90Al10Co mixture iso-thermally treated at different temperatures. b) Representative image of 90Al10Co pigments synthesized at different temperatures. c) CIE-L*a*b* coordinates of 90Al10Co pigments iso-thermally treated at different temperatures. d) CIE-L*a*b* colorimetric coordinates of different cobalt content compositions. A reference cobalt aluminate commercial pigment is used as reference for the colorimetric coordinates.

Figure 5. Confocal Raman Microscopy of an isolated single pigment particle 90Al10Co synthesized at 1200°C for 1 hour: a) Optical microscopy micrograph. b) Raman image

in which colour intensity evidences Raman intensity of the main F2g Mode for CoAl_2O_4 phase (c) Raman spectra of 90Al10Co pigment and Raman spectra of $\alpha\text{-Al}_2\text{O}_3$ and CoAl_2O_4 references.

Figure 6. FESEM of the 90Al10Co pigment treated at 1200°C: a) general view of 90Al10Co in order to show that the coating is complete, b) enlarged general view of 90Al10Co sample with triangular nanoparticles, c) detail of triangular shaped 2D particles, and d) detail of surface coalescence which shows 2D structures with a hole in the middle.

Figure 7. Atomic force microscopy images of 90Al10Co sample (a), detail of 90Al10Co sample (b, d) and roughness (c, e).

Figure 8. a) Schematic of the lowest energy surfaces of the CoAl_2O_4 crystal. b) Schematic of morphology of the CoAl_2O_4 triangular shaped particles on $\alpha\text{-Al}_2\text{O}_3$ surface. c) Schematic evolution of the cobalt nanoparticles coalescence before the spinel formation.

Figure 9. NIR response of 2D shell pigments with different cobalt content: a) UV-VIS NIR reflectance. b) R^* in the spectral range 700-2500 nm. c) Solar reflectance spectra. d) SR in the spectral range 700-2500 nm. The representation of R^* and SR is considered versus the formulated Co_3O_4 wt. % amount. The commercial pigment used as reference corresponds to an equivalent 44 wt. % of Co_3O_4 .

HIGHLIGHTS

- Safety method to obtain nanostructured surfaces onto microparticles as supports.
- Nanoparticles are securely anchored to the microparticles by using a dry dispersion method.
- Two mechanisms of 2D CoAl_2O_4 crystallization over $\alpha\text{-Al}_2\text{O}_3$ surface are observed.
- The core-shell reduces the amount of required cobalt and their toxic effects.
- Solar reflectivity enhances by achieving values higher than 70% in the NIR range.