Blue $CoAl_2O_4$ Particles Prepared by the Sol−Gel and Citrate−Gel Methods

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Bright blue $CoAl_2O_4$ particles were prepared by the sol−gel and citrate−gel methods using aluminum *sec*-butoxide, cobalt salts, and citric acid as oxides precursors. Both methods start from sols of the precursor alkoxides and salts, and involve formation of homogeneous solid intermediates, reducing atomic diffusion processes during thermal treatment. This important feature results in a substantial lowering of the time and temperature needed for the formation of the desired compounds. The stages of the formation of $CoAl_2O_4$, as well as the characterization of the resulting compounds were done using XRD, FTIR, UV−VIS, SEM, and TGA/DTA techniques. The structure, coloration, particle size, and temperature of formation of the resulting $CoAl_2O_4$ phases were found to depend on the precursors and methods used for preparation and the calcination temperature. The lowest temperature for preparation of the blue cobalt aluminate of about 700 °C was obtained using the citrate−gel method. This temperature is much lower than that needed for preparation of the compound through traditional solid-state reactions (above 1000 °C).

1. Introduction

Cobalt aluminate powders have been widely used as inorganic ceramic blue pigments (Thénard's Blue). Cobalt aluminates are also of great interest in the field of heterogeneous catalysis.[1,2] $CoAl_2O_4$ have the structure of a normal spinel in which Co^{II} ions are accommodated in tetrahedral positions while Al^{III} ions are in octahedral positions. This compound has been prepared by different methods: reaction between Co and Al oxide powders at high temperature (800 °C),[3] resulting in a blackish-blue compound, or to 1200−1300 °C,[4] resulting on a bright blue pigment; coprecipitation of mixed aqueous solution of Co and Al salts and subsequent calcination to 400 and 800 °C, producing a very dark blue-green colored oxide material;[5] calcination of alumina powder soaked in cobalt nitrate solution to 1200 °C, giving blue cobalt aluminate.[2] The compound was also prepared by calcination of powdered Al_2O_3 coated with a thin film of metallic cobalt at 1000 °C (20 h), giving the characteristic bright blue color of cobalt aluminate.[6] Similar preparation and results were reported, using oriented single crystals of α- and γ-Al_2O_3 instead of powdered Al_2O_3 oxide.[7]

Sol−gel preparations start from solution of the appropriate precursors and salts (usually alkoxides), that after hydrolysis and condensation form homogeneous oxide networks. The sol−gel method offers a great advantage in the preparation of mixed oxide compounds as compared with the traditional solid-state method.[4] The formation of a gel with a high degree of homogeneity reduces drastically the need of atomic diffusion during the calcination process, allowing therefore the formation of the desired phases at much lower temperatures and shorter calcination times that in solid-state reactions. The sol−gel method allows tailoring of the properties of the resulting compounds by the correct choice of the precursors and preparation conditions. The sol−gel method was used to prepare $CoAl_2O_4$ doped mullite composites.[8] The preparation of high surface $CoAl_2O_4$ spinel powder by an alkoxide route was recently reported.[9] The compound was prepared by a double alkoxide precursor and calcined at 400 °C for 3 h; however, neither the coloration, nor a detailed characterization of the resulting compound were given.

The citrate−gel method allows preparation of highly dispersed mixed oxides.[10,11] The method involves the formation of a mixed-ions citrate that due to the three ligand nature of the citrate, forms a transparent three-dimensional network upon drying (gel). The pyrolysis of this gel results in a homogeneous mixed oxides. The method was widely used to prepare multicomponent oxides, for example superconductors.[12,13]

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In this paper the sol−gel and citrate−gel methods were applied to prepare mixed Co−Al oxide particles in an attempt to reduce the temperature of preparation and calcination times. The resulting powders were characterized by XRD, FTIR and UV−VIS reflection spectra. SEM images of the resulting particles are also given. TG/DTA measurements were used to follow the calcination of the precursors to the final oxide compound.

2. Experimental Section

2.1. Materials. Aluminum *sec*-butoxide (95%), cobalt acetate tetrahydrate (99%), and aluminum nitrate nonahydrate (99%) are from Fluka, cobalt nitrate hexahydrate (98%) and citric acid (99%) are from Aldrich Chemicals, 2-butanol (98%) was from Merck. Doubly distilled water was used for all preparations.

2.2. Preparation of Samples. Blue cobalt aluminate particles were prepared from aluminum *sec*-butoxide (ASB) and cobalt acetate (sample SG1). In sample SG2 cobalt acetate was replaced by cobalt nitrate. The same compound was also prepared using the Citrate−Gel method (sample CG1). Samples were placed in a cold oven and heated progressively to the desired temperature for a very short calcination of about 5 min.

Samples SG1 and SG2. SG1: A 50% solution of ASB in BuOH was added dropwise to a 0.9796 M aqueous solution of cobalt(II) acetate under continuous stirring. A thick paste was obtained having a purple coloration (redish pink for SG2 sample). After complete drying at 100 °C, the powder was thermally treated to up to 1000 °C. SG1 samples were prepared using different Co:Al ratios ($Co_{3-S}Al_SO_4$ with $1.71 \leq S \leq 2.57$). The brightest blue coloration was obtained for $S = 2.25$, and all measurements were done on this composition. In sample SG2 cobalt acetate was replaced by $Co(NO_3)_2$. Samples were prepared with $S = 2.25$ composition.

Sample CG1. Citric acid was added to an aqueous solution of Co and Al nitrates in the Me:citric acid ratio of 1:1. The solution was allowed to evaporate (at 100 °C) to dryness. A sponge-like solid structure was obtained (due to the partial release of nitric−nitrous vapors during the formation of the citrate gel). The sample was then heat treated to up to 1000 °C. CG1 samples were also prepared with $S = 2.25$ composition.

2.3. Characterization. X-ray diffraction measurements were carried out on a Philips PW1710 diffractometer using a PW1820 goniometer. The diffraction patterns were recorded with a step-size of $2\theta = 0.02°$ and 0.5 s/step. Thermogravimetric analysis were carried out on a Seiko SSC/5200 (TG-DTA 320U). Measurements were done in air or nitrogen flow of 50 mL/min using a heating rate of 10 °C/min. UV−VIS spectra were recorded on a Varian 2300 spectrophotometer. FTIR spectra were recorded on a Nicolet 20SXC spectrometer. SEM pictures were obtained on a Zeiss DSM-950.

3. Results

3.1. UV−VIS Spectra of the Samples. The coloration of the calcined powders was found to be strongly dependent on the temperature of the heat treatment and on the stoichiometry of Co and Al in the $Co_{3-S}Al_SO_4$ sample. SG1 samples heated to 1000 °C with *S* values smaller than 2, exhibited a dark green coloration, changing progressively to bright-blue as *S* values are increased. On the other hand, samples heated below the temperature of formation of the blue $CoAl_2O_4$ phase showed the same dark green coloration of cobalt-rich samples.

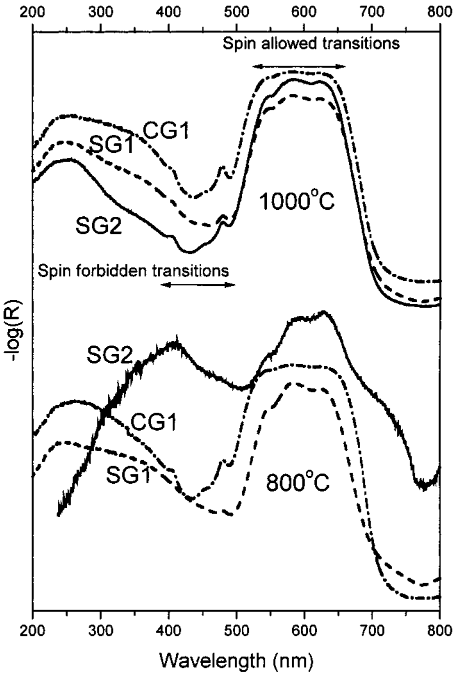

Figure 1. UV−VIS reflectance spectra of $Co_{3-S}Al_SO_4$ samples ($S = 2.25$) calcined to 800 and 1000 °C.

Co^{II} ions with configuration $3d^7$ have, in tetrahedral or octahedral coordination, three electronic transitions allowed by the spin[4] and three transitions that are spin-forbidden in the UV−VIS range. These transition can be assigned to $^4A_2(F) \rightarrow {}^4T_1(P)$ and $^4A_2(F) \rightarrow {}^2T(G)$ respectively.[2] The spectra of $Co_{3-S}Al_SO_4$ samples SG1, SG2 and CG1 with $S = 2.25$ prepared here at 1000 °C (Figure 1) showed a three band absorption pattern around 543, 580, and 630 nm, which is characteristic for tetrahedral Co^{II} transitions allowed by the spin. The spin-forbidden transition were observed as small peak or shoulders around 408, 447, and 479 nm. The spectra obtained for cobalt aluminate samples are consistent with those obtained from particles prepared by the traditional solid-state method[4] or with the spectra of $CoAl_2O_4$ grown by calcination of a thin layer of metallic cobalt deposited on an oriented surface of a Al_2O_3 single crystal.[7] A very similar pattern was observed by Sales et al.[8] for $CoAl_2O_4$−mullite composites. Harrison et al.[14] reported on the introduction of Co^{II} salts in post-doped silica sol−gel glasses, after calcination at 900 °C the samples gave the same pattern shifted slightly to the red. Similar results were reported by Alarcon et al.[15] for $LiCoTi_3O_8$ samples prepared by solid-state procedures and heated to 900−1000 °C. The spectrum obtained was shifted about 50 nm to the red.

The temperature of preparation plays also an important role in the coloration of samples. SG1 ($S = 2.25$)

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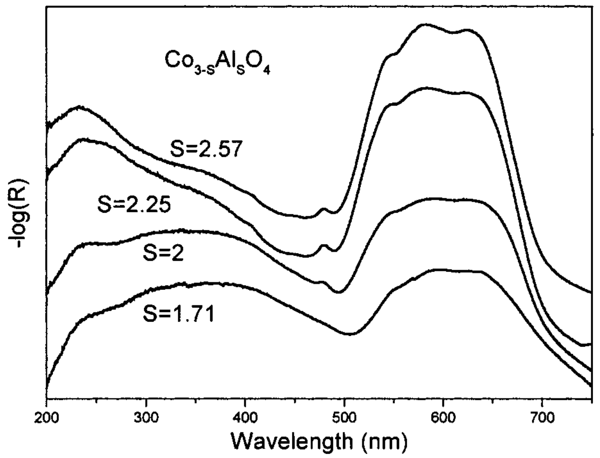

Figure 2. UV−VIS reflectance spectra of SG1 samples $Co_{3-S}Al_SO_4$ with different S values.

samples heated below 800 °C showed a dark green coloration. At 800 °C, the compound turns deep blue and the spectra shows only the typical triplet of Co^{II} in tetrahedral coordination. In the case of SG2 and CG1 samples (both with $S = 2.25$) the same behavior is observed, differing only in the temperature of formation of the blue phase which is about 1000 and 700 °C for SG2 and CG1 samples, respectively. The spectra of all three samples at 800 °C are shown in Figure 1.

The change in coloration in SG1 samples calcined at 1000 °C and having different S values ($Co_{3-S}Al_SO_4$) can be guessed from a simple observation of the UV−VIS reflectance spectra (see Figure 2). In addition to the triplet at 540−630 nm, a broad absorption band from 300 to 400 nm is observed in cobalt-rich samples ($S <$ 2), which is responsible for the dark green coloration of these samples. The intensity of this band decreases as the S value is increased and the sample turns bright blue. The band at 300−400 nm is possibly due to octahedrally coordinated Co^{III} species and is also observed, with much lower intensity, in stoichiometric $CoAl_2O_4$- and Al-rich samples. In Co-rich samples ($S <$ 2) the effect can be due to the formation of Co_3O_4 in addition to $CoAl_2O_4$ with the excess of cobalt in the sample. In stoichiometric $CoAl_2O_4$ or Al-rich samples, it can be due to a partially inverted spinel structure in which a very small amount of Co^{III} ions occupy octahedral sites in the spinel structure. The faster condensation rate of the aluminum alkoxide as compared with Co precursors may also lead to the formation of a small amount of cobalt oxide Co_3O_4 (octahedral Co^{III} and tetrahedral Co^{II} species) at the surface of aluminum-rich particles. Samples with S values larger than 2.25 remain blue but lose some of the intensity of the color. This can be explained by the formation of white Al_2O_3 from the excess of Al in the samples. It is important to note that the broad band at 300−400 nm is not observed in SG2 ($S = 2.25$) sample which exhibits a brighter blue coloration as compared with SG1 ($S = 2.25$) sample.

3.2. Thermogravimetric Analysis. TGA-DTA analysis was carried out on the samples during the formation of the particles for SG1, SG2, and CG1 samples (see Figure 3). Sample SG1 exhibits two endothermic transitions at 77 and 230 °C which are related to the dehydration of cobalt acetate. A very strong and sharp exothermic peak around 315 °C is due to the combustion of the acetates. Sample SG2 exhibits two endothermic peaks around 94 and 265 °C which are due to the dehydration and decomposition of cobalt nitrate, respectively. Sample CG1 gave an exothermic peak at ~170 °C followed by an endothermic peak around 210 °C. Those transitions are related to the combustion of uncomplexed citric acid and the decomposition of nitrates remaining in the sample, respectively. At 480 °C a broad and large exothermic peak is observed which is due to the combustion of the Co and Al citrates. $CoAl_2O_4$ phase formation is observed clearly around 700 °C in CG1 sample (Figure 3). In samples SG1 and SG2, however, the phase transformation occurs progressively without a sharp transition. This can be explained by a much higher homogeneity of the CG1 sample which undergo a very rapid phase transformation without the need of atomic diffusion. These observations come in agreement with the temperatures of the $CoAl_2O_4$ phase formation observed by a color change (from black to blue) in the different samples.

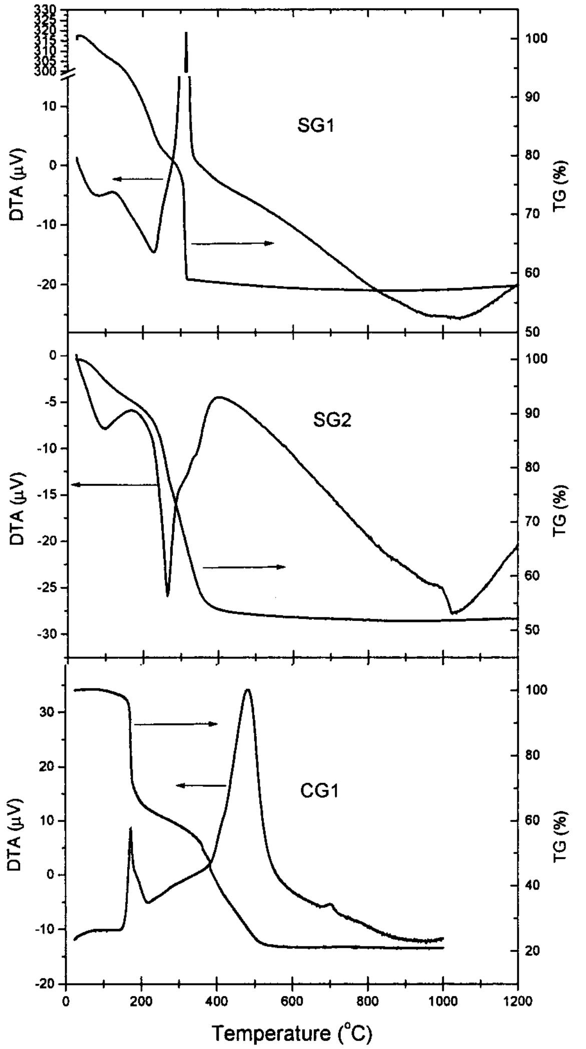

Figure 3. TGA-DTA of the preparation of $CoAl_2O_4$ particles samples SG1, SG2, and CG1 carried out in dynamic air.

3.3. Crystallographic Analysis. Cobalt aluminate ($CoAl_2O_4$) has normal spinel structure with Co^{II} and Al^{III} ions in tetrahedral and octahedral positions, respectively. According to the literature the most stable cobalt

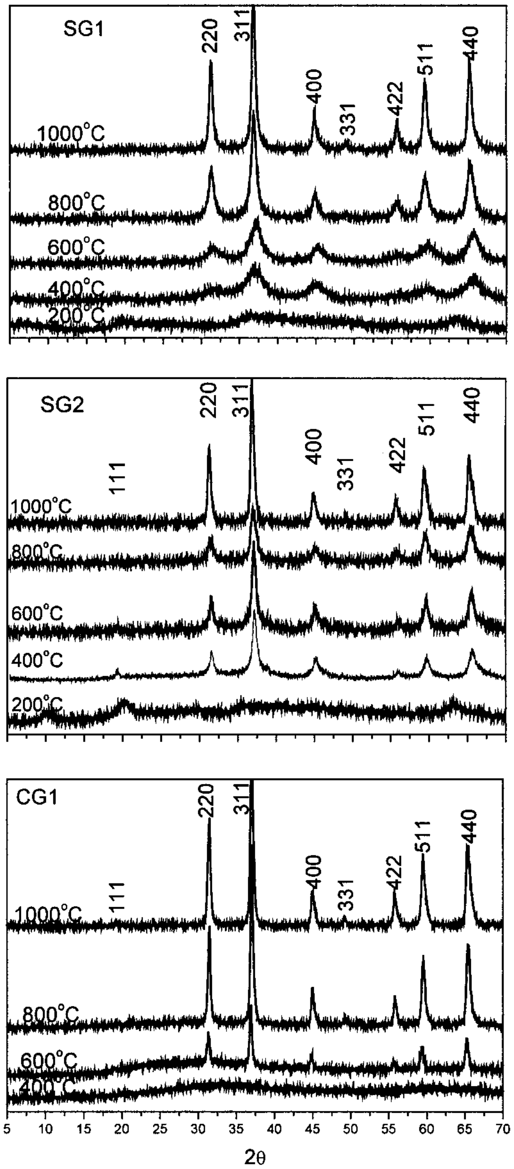

Figure 4. XRD patterns of SG1, SG2, and CG1 $CoAl_2O_4$ particles heated at different temperatures.

oxide at room temperature is the mixed-valence Co_3O_4 which has the same spinel structure as the aluminate. Above 950 °C, the oxide is reduced to CoO. In the preparation of mixed Co:Al oxides reported here divalent cobalt precursor are used, which are partially oxidized above 400 °C, giving the stable Co_3O_4 phase. Cobalt oxide is then reduced between 700 and 1000 °C, depending on the preparation technique. This process is believed to be accompanied by the formation of the blue $CoAl_2O_4$ phase. SG1, SG2, and CG1 samples heated at 1000 °C showed the same X-ray diffraction patterns (Figure 4) corresponding to the $CoAl_2O_4$ spinel phase (*Fd*3*m* with lattice size of 8.104 Å, JCPDS 44-0160).

XRD patterns of the samples calcined at different temperatures give us information on the intermediate stages of the formation of $CoAl_2O_4$. The Co_3O_4 phase can clearly be observed in SG1 and SG2 samples calcined at 400 °C. The $CoAl_2O_4$ phase appears only at 800 °C in SG1 and at 1000 °C at SG2. The latter can be distinguished from the Co_3O_4 phase by the observation of a new small line at $2\theta = 49$, which belongs to $CoAl_2O_4$ (see Figure 4). These results are agreement with the visual observation of the coloration of the samples calcined at different temperatures.

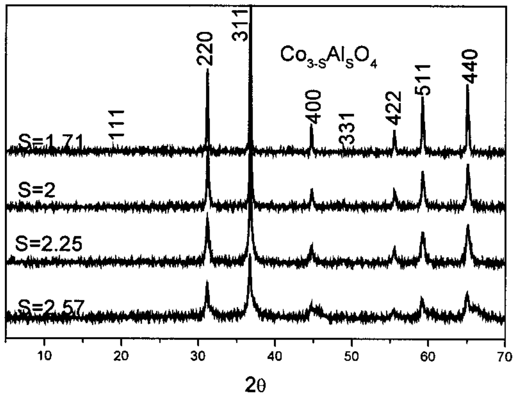

Figure 5. XRD patterns of $CoAl_2O_4$ particles prepared with different *S* values.

The size of the particles at different calcination temperatures can also be deduced from the XRD patterns and are quite different in both SG1 and SG2 samples. At 400 °C SG2 exhibits much narrower diffraction lines than SG1, denoting a larger particle size (~3 nm for SG1 and ~8 nm for SG2). Subsequent heating to higher temperatures resulted in the increase of the particle size of the powders reaching both, at 1000 °C, approximately the same particle size (~16−19 nm).

The case of CG1 sample (citrate−gel) is completely different from the SG1 and SG2 samples. At 400 °C the compound is completely amorphous, since the citrates have not been burned yet. At 600 °C very narrow bands of Co_3O_4 are observed. At 800 and 1000 °C a highly crystallized $CoAl_2O_4$ phase is obtained (~20−25 nm). The particle size of CG1 sample does not grow substantially from 600 to 1000 °C.

Particle sizes were calculated from the XRD patterns shown in Figure 4 using Scherrer's equation.

Samples prepared with *S* values above 2 showed in addition to $CoAl_2O_4$, a second phase that can be assigned to σ-Al_2O_3, having also a spinel structure with a lattice size of 7.9448 Å (JCPDS 47-1292). On the other hand, on samples prepared with an excess of cobalt (*S* values below 2) a second phase, in addition to $CoAl_2O_4$, is observed which can be assigned to Co_2AlO_4 or Co_3O_4. Narrower diffraction lines were observed for cobalt-rich samples as compared with stoichiometric or aluminum rich samples denoting a higher degree of crystallization. See Figure 5 and a detail of the (440) line in Figure 6. It is important to note that due to the similar ionic radius of Co^{3+} and Al^{3+}, it is quite difficult to distinguish between the diffraction lines of Co_3O_4, Co_2AlO_4, and $CoAl_2O_4$. All three compounds have the same spinel cubic (*Fd*3*m*) structure differing only slightly in the size of the lattice: 8.104 Å for $CoAl_2O_4$ (JCPDS 44-0160) and 8.0837 Å for Co_3O_4 (JCPDS 42-1467) or 8.086 Å for Co_2AlO_4 (JCPDS 38-0814).

3.4. FTIR Measurements. FTIR measurements were used to identify and characterize the resulting spinel powders. All three samples calcined at 1000 °C showed almost the same FTIR spectra. Four lines are observed around 505, 550, 597, and 670 cm^{-1}, respectively, which are attributed to the vibrational bands of $CoAl_2O_4$. This pattern is typical for a normal spinel

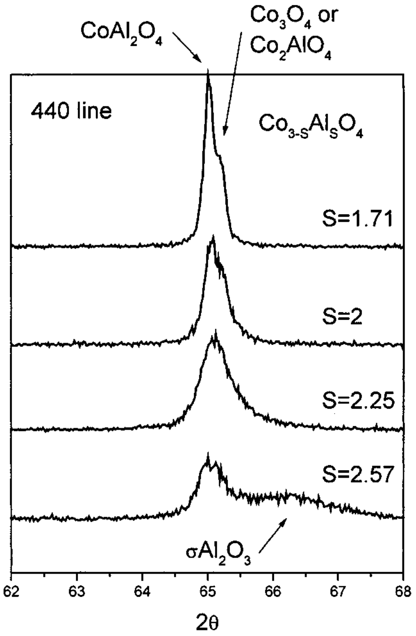

Figure 6. Detail of the XRD patterns showed in previous figure.

compound and specifically fit with that of $CoAl_2O_4$ spectra as reported by Tarte et al.[16] (see Figure 7). The band at 505 cm^{-1}, however, appears with a higher intensity than that at 550 cm^{-1}, in opposition to that observed by Tarte et al. The FTIR pattern (intensity ratios) obtained here for $CoAl_2O_4$ is very similar to that obtained by Preudhomme et al.[17] for $MgAl_2O_4$ normal spinels differing only slightly in the position of the bands. FTIR measurements were also very helpful to follow the formation of $CoAl_2O_4$ from the precursors. Figure 7 shows also the FTIR spectra of SG1, SG2, and CG1 samples respectively, calcined at different temperatures. Samples SG1 and SG2 heated to 600 °C exhibit two broad bands around 560 and 680 cm^{-1}, respectively. These bands can be assigned to cobalt oxide as observed by Busca et al.[18] for commercially prepared Co_3O_4. Heating the samples to 800 and 1000 °C resulted in the formation of narrower $CoAl_2O_4$ bands. The Co_3O_4 line around 560 cm^{-1} decreases in intensity as temperature is raised in both SG1 and SG2 samples. The bands obtained here for blue cobalt aluminate are quite different from those reported by Busca et al.[5] for $CoAl_2O_4$ samples prepared by coprecipitation of Co and Al salts and calcined to 400−800 °C, which are much more in agreement with Co_3O_4 bands. One significant difference found between samples SG1 and SG2 is the width of the FTIR bands. SG2 sample exhibited much narrower lines as compared with SG1 sample at a given temperature. At 1000 °C, however, both samples have similar bandwidth. Citrate gel prepared samples (CG1) is amorphous at 600 °C, while at 800 °C has already the $CoAl_2O_4$ structure.

3.5. SEM Images. SEM images of the $CoAl_2O_4$ particles SG1, SG2, and CG1 prepared here are shown in Figure 8. The obtained powders were ground manually in an agate mortar prior to the observation in the electron-microscope. Big particles around 1−3 μm are observed which are composed from much smaller agglomerated particles (0.1−0.2 μm) for SG1 and SG2 samples. Sample CG1, however, exhibits big particles ranging from 1 to 20 μm.

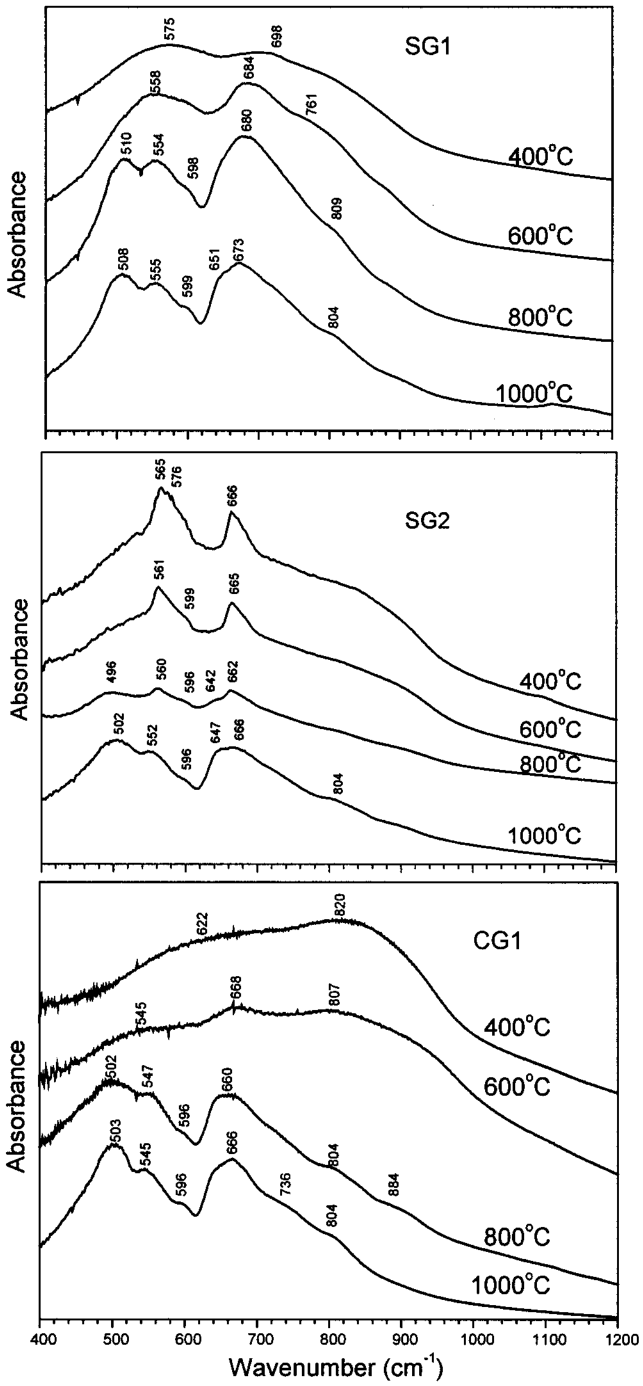

Figure 7. FTIR spectra of samples SG1, SG2, and CG1 calcined at different temperatures.

4. Discussion

We report here on the preparation and characterization of $CoAl_2O_4$ using the sol−gel and citrate−gel methods. The resulting compounds were characterized by UV−VIS spectroscopy, XRD and FTIR.

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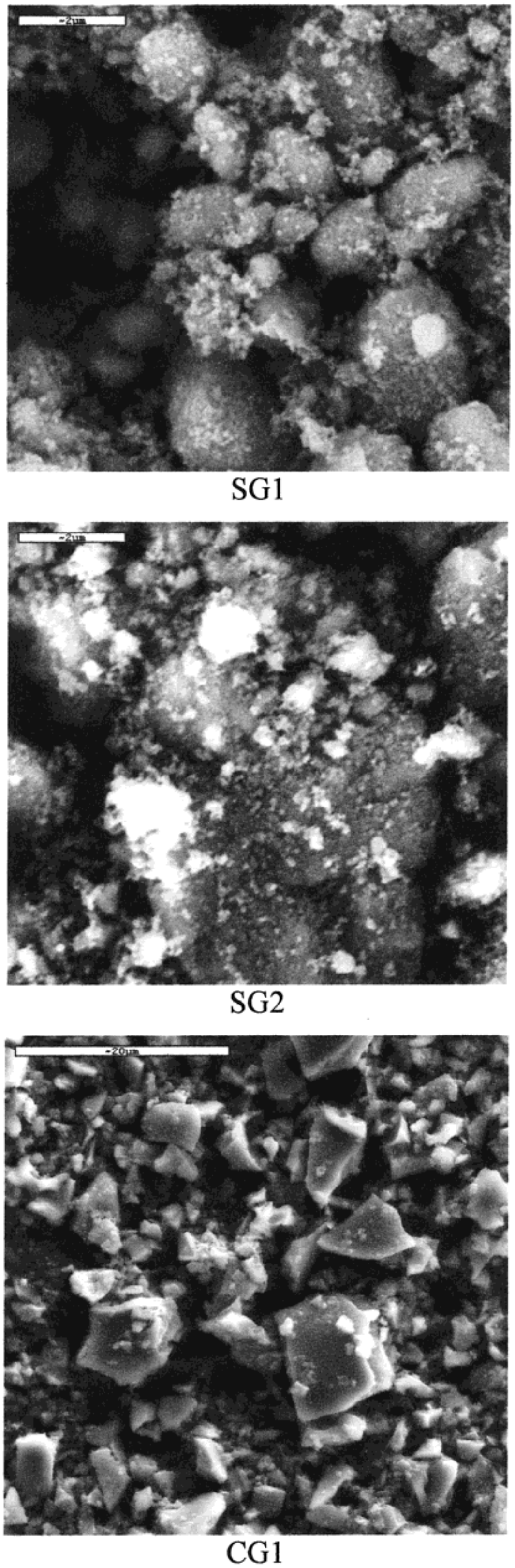

SG1

SG2

CG1

Figure 8. SEM Images of $CoAl_2O_4$ particles of samples SG1, SG2, and CG1 calcined at 1000 °C.

Divalent cobalt salts, used as cobalt precursor, were partially oxidized at low temperature (400−600 °C) to Co^{III} forming the mixed-valence spinel oxide Co_3O_4 below 400 °C in SG1 and SG2 and around 480 °C for CG1. Co^{III} is then reduced again to Co^{II} around 700−1200 °C when $CoAl_2O_4$ is formed. The temperature of calcination needed to obtain bright blue $CoAl_2O_4$ was between 700 and 1000 °C depending on the precursors used for preparation. The brightest blue coloration was obtained for SG2 sample heated to 1000 °C. The citrate−gel method gave the lowest calcination temperature of about 700 °C. This temperature is much lower than that needed to produced blue $CoAl_2O_4$ by solid-state procedures, which is usually above 1000 °C.

Samples prepared using cobalt acetate or cobalt nitrate precursors (SG1 and SG2) are decomposed below 400 °C when the formation of Co_3O_4 oxide starts. Neither of the samples exhibited a sharp transition to the blue $CoAl_2O_4$ phase, which occurred progressively as shown by the TGA/DTA measurements. By the development of the blue coloration (UV−VIS spectra and visual determination), however, one can observe that the transition in samples prepared with cobalt acetate (SG1) occurs around 800 °C, while in samples prepared with cobalt nitrate (SG2) the transition occurs around 1000 °C. This can be explained by the differences in oxidative and reducing properties of the nitrate and acetate anions respectively, during their thermal decomposition. Oxidative conditions during the formation of the spinel phase can lead to a higher degree of inversion in the Co−Al spinel structure, resulting on the need of higher temperatures to reduce Co^{III} ions to form $CoAl_2O_4$. Citrate−gel sample (CG1) was completely amorphous at 400 °C as the combustion of the citrates occur only around 480 °C (from TGA/DTA). At 600 °C the black cobalt oxide Co_3O_4 is obtained, which is reduced at 710 °C to the blue $CoAl_2O_4$. Further heating to up to 1000 °C did not increase neither the crystallinity nor the color strength of the resulting blue $CoAl_2O_4$ powder.

The particles size of the resulting compounds depend on the method of preparation and the temperature of the heat treatment. The formation of a transparent and very homogeneous gel in the citrate−gel preparation promoted the formation of larger particles of blue $CoAl_2O_4$ already at 710 °C. The particles did not grow substantially by heat treatments at higher temperatures. The sol−gel preparations using aluminum *sec*-butoxide and cobalt salts, due to the fast condensation of the precursors, lead to less homogeneous dry intermediate which produced smaller particles upon calcination at low temperatures (400 °C) as calculated from XRD patterns. The particles grow rapidly as the temperature of the heat treatment is raised, reaching almost the same size as the citrate−gel particles when heated at 1000 °C. One point that is not fully understood is why the SG1 sample at 400 °C has a much smaller particle size than that of SG2 sample at the same temperature. At 1000 °C, both samples reach approximately the same particle size.

The particle size of the different samples calcined at 1000 °C as seen in the SEM pictures are quite different from those estimated from the XRD patterns. The particles observed in SEM pictures are composed from very small particles (<100 nm), which are responsible for the widening of the XRD patterns. Sol−gel preparations gave agglomerates (1−3 μm) composed from small particles (smaller than 0.1−0.2 μm) while citrate−gel preparations gave much larger and well crystallized particles (1−20 μm).

5. Conclusions

In this work, blue $CoAl_2O_4$ particles were prepared using the sol−gel and citrate−gel procedures. The different methods of preparation gave particles with different properties (coloration, particle size, etc.). The temperature of formation of the blue $CoAl_2O_4$ phase was determined among others by the nature of the precursors used for preparation. Because of the higher homogeneity of the precursor gel, the citrate−gel procedure allowed a significant reduction of the calcination temperature to about 700 °C, giving large particles of 1−20 μm. On the other hand the fast gelation observed in the sol−gel method allowed the preparation of small particles of 0.1−0.2 μm at higher calcination temperatures of 800−1000 °C. Both, the sol−gel and the citrate−gel methods described here can also be applied for the preparation of a large family of aluminates.

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