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# Low Temperature Soft Chemical Synthesis of Bright Blue $CoAl_2O_4$ Spinel Particles

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## Abstract

*Present work reports the preparation of bright blue $CoAl_2O_4$ spinel particles by low temperature soft chemical route using urea or glycine as fuel in this paper. The characterization of the resulting powder was done using x-ray diffraction (XRD), particle size analysis and scanning electron microscopic (SEM) techniques. Pure $CoAl_2O_4$ spinel particles were prepared at relatively low temperature using this soft chemistry route at a very short duration (< 10 minutes) which is also very simple than other techniques such as solid state reaction, ceramic methods and so on. From the particle size analysis, it was found that the spinel particles with low diameter (below 35 μm) were formed. The SEM photographs showed the formation of fluffy morphology with porous structure.*

***Keywords****: Cobalt aluminate spinel, low temperature soft chemistry route, XRD, SEM.*

## Introduction

The $CoAl_2O_4$, the ceramic pigment known as cobalt blue, has been recognized since prehistoric times, and has often attracted the interest of scientists[1]. Cobalt aluminates were used in technical applications, such as chemical sensors, ion conductors or heterogeneous catalysts[2]. Organic ligand capped $CoAl_2O_4$ hybrid transparent nano pigment, which has a particle size less than 8 nm with well-stabilized single nanocrystals was prepared for application in metallic finishing and in high-end optical filters[3]. They were also important materials for heterogeneous catalysis in areas such as the $CO_2$ reforming of methane[4]. In thin-film form, cobalt aluminates recently became interesting as a light filter for automotive lamps[5]. Lamps with tungsten wire emit a yellowish light because the intensity of the emitted light peaks in the near-IR range (~1 μm) due to the relatively low temperature of the tungsten filament. To increase the visibility of vehicles it would be better if the emitted light exhibited a spectral distribution which resembles that of daylight. One way to achieve this is to block selectively, at least in part, the long wavelength radiation which is emitted from the hot tungsten wire. The $CoAl_2O_4$ is quite suitable for this purpose because it exhibits a characteristic absorption in the 500-600-nm range[6], which gives the coating its typical bright

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blue color (royal blue). Consequently, the color temperature of the wire is shifted to higher temperatures and the emitted light resembles daylight to the human eye[7].

Various techniques were reported to prepare the $CoAl_2O_4$ spinel particles. The conventional method for the preparation of these pigments is by the solid state reaction (ceramic method) using corresponding metal salts like oxides, carbonates, etc.[8] This requires high temperature (1000–1400°C) and long processing time (several hours to days). The end products are usually coarse and inhomogeneous which render them inapplicable. They require further processing like wet or dry milling to produce fine powders[9]. Other methods, such as sol-gel processing[10-11], malonate processing[12], polyol processing[13], hydrothermal processing[14], co-precipitation method[15], etc. were also reported in the literature for the preparation of the $CoAl_2O_4$ spinel particles in which long processing was involved. In this paper, we report the preparation of $CoAl_2O_4$ spinel particles by cost-effective low temperature soft chemical route (combustion synthesis) using glycine and urea as fuels. This method has been used successfully for the synthesis of fine oxide materials[16-17]. In this study, cobalt blue (cobalt aluminate) pigment particles were synthesized by solution combustion process and the characteristics of the synthesized particles were studied and discussed.

## Experimental Methods

$CoAl_2O_4$ spinel particles were prepared by combustion process using urea or glycine as fuels. The combustion method involves the combustion of saturated aqueous solution containing stoichiometric quantities of cobalt nitrate, aluminium nitrate and fuel (urea or glycine). The appropriate quantities of the precursor nitrate salts (cobalt nitrate and aluminium nitrate) were calculated according to the concepts of propellant chemistry[18-19], taken in a silica crucible and dissolved in distilled water. Calculated amount of fuel (urea or glycine) was added to the above solution with continuous stirring and homogenized well. The stoichiometric proportion of precursor materials used for the synthesis of $CoAl_2O_4$ spinels is indicated in Table 1. The oxidizer : fuel ratio was calculated based on oxidizing (O) and fuel (F) valencies of the reactants keeping O/F = 1 as reported previously[20-21]. The aqueous redox solution containing metal nitrates and fuel (urea or glycine) when introduced into a muffle furnace preheated at 600°C, boils, froths, ignites and catches fire (at a high temperature 1100 ± 100°C)[21]. At this temperature, the metal nitrates decompose to metal oxides and oxides of nitrogen, and hence act as oxidizer for further combustion, which leads to a voluminous, foamy combustion residue in less than 10 minutes. The flame persisted for about 1 minute. The foam was then lightly ground in a glass basin with porcelain pestle to obtain fine particles. The procedure is explained schematically in Fig. 1.

The stoichiometric redox reactions involved in the combustion synthesis of $CoAl_2O_4$ spinels can be represented by the following theoretical equations (1) and (2).

$$Co(NO_3)_2 + 2Al(NO_3)_3 + 6.66NH_2CONH_2 \rightarrow CoAl_2O_4 + 6.66CO_2 + 10.66N_2 + 13.32H_2O \quad (1)$$

$$Co(NO_3)_2 + 2Al(NO_3)_3 + 4.44NH_2CH2COOH \rightarrow CoAl_2O_4 + 8.88CO_2 + 6.22N_2 + 11.10H_2O \quad (2)$$

***Table 1**: Stoichiometric proportion of the precursor materials used for the synthesis of $CoAl_2O_4$ powder.*

| Weight of $Co(NO_3)_2$ (g) | Weight of $Al(NO_3)_3$ (g) | Weight of glycine (g) | Weight of urea (g) | Weight of synthesized $CoAl_2O_4$ powder (g) | weight loss at 800°C (%) |
|---|---|---|---|---|---|
| 3.66 | 8.52 | -- | 5.0 | 2.0088 | 0.91 |
| 3.66 | 8.52 | 4.0 | -- | 1.9190 | 1.92 |

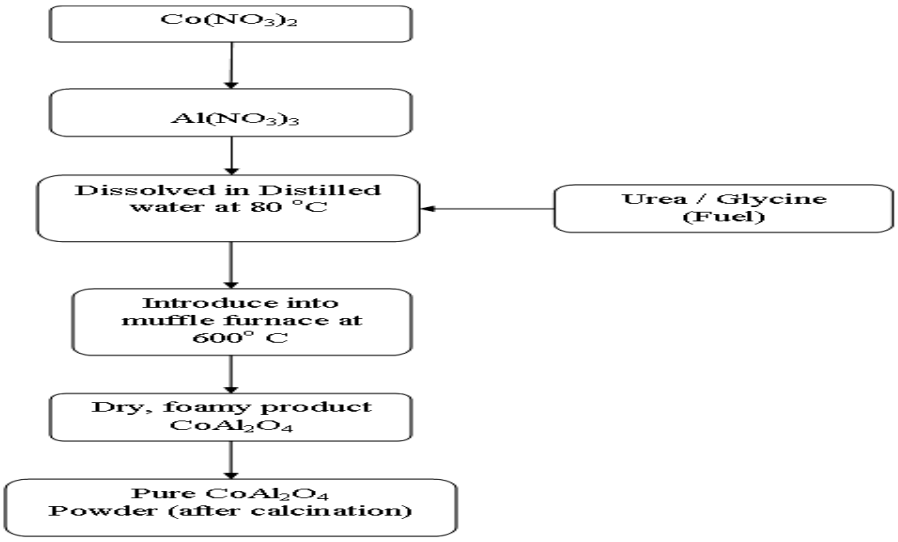


***Figure 1**: Flow chart for the preparation of $CoAl_2O_4$ powder by combustion synthesis.*

The as-synthesized powder was taken in clean alumina crucibles and calcined in air at 800°C for 4 hours to remove the deposited carbon and the unreacted organic residues and to get phase pure compound[22]. Calcination of the as-synthesized powder implies a very significant weight loss (0.9–1.9%). The calcination data is indicated Table 1. The powder XRD study was carried out using a Shimadzu XRD 6000 X-ray diffractometer at a scan speed of 5 deg/min using $CuK_\alpha$ radiation. The crystallite sizes of the ceramic powders were calculated by Scherrer's formula. The particle size of the powder was measured using a Horiba Laser Scattering Particle Size Analyzer (LA-910) using triple distilled water as medium. The morphology of the particles was studied by means of JEOL Model JSM-6360 scanning electron microscope.

## Results and Discussion

Figure 2 shows the XRD patterns for the $CoAl_2O_4$ powder prepared by combustion synthesis using urea and glycine as fuels and calcined at 800° C for 4 hours. All the peaks in the XRD patterns are very sharp showing the well crystalline behavior of heat treated powders. The identified phases present in the XRD patterns of $CoAl_2O_4$ are of cubic spinel-

type (JCPDS No. 44-0160). No impurity phases were detected in the XRD patterns of $CoAl_2O_4$ powder prepared using both urea and glycine as fuels. From the XRD data, it was found that 100 % crystallization of $CoAl_2O_4$ could be achieved by combustion technique. The presence of a spinel phase, which was developed at a relatively low temperature, indicates the advantage of soft chemical synthesis applied here. The formation of $CoAl_2O_4$ was also in accordance with the observation of the intense blue coloration of the corresponding oxide powder. However, it had been reported that $CoAl_2O_4$ powder was prepared by a solid state reaction greater than 1000°C after prolonged annealing with extended grinding[8].

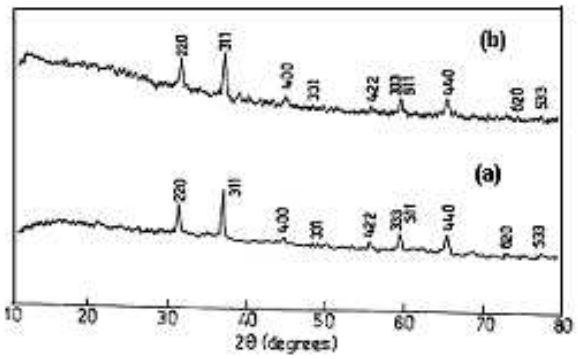


***Figure 2:*** *XRD patterns obtained for the $CoAl_2O_4$ powder prepared by combustion synthesis using (a) urea and (b) glycine as a fuel.*

The lattice parameters were calculated from 2θ peaks in the XRD pattern. The unit cell volumes calculated for $CoAl_2O_4$ remained almost equal. The theoretical density was calculated using the lattice parameters with formula[23].

$$D_{th} = z\frac{M}{N \times V} \tag{3}$$

where 'M' (in atomic-weight units) is the mass of one unit of the chemical formula, 'z' is the number of such chemical units in one unit cell of the crystal, 'N' is the Avagadro's number and V (in $Å^3$) is the volume of the crystalline unit cell as determined by X-ray diffraction. These values were also agreed well with the reported data. The crystallite sizes of the $CoAl_2O_4$ powder were calculated from the most intense XRD peak using Scherrer formula[24].

$$D = \frac{0.9 \times \lambda}{\beta \times \cos\theta} \tag{4}$$

where, D is crystallite size in nm, λ is the radiation wavelength (λ = 1.5418 Å), θ is the diffraction peak angle and β is the broadening of the line (half width at most intense peak in radian). The crystallite size of the particles was found to be in the range of 14-20 nm for the powder samples calcined at 800°C for 4 hours. This is in agreement with previous report about the crystallite size of sol-gel prepared $CoAl_2O_4$[25]. The crystallographic parameters obtained on $CoAl_2O_4$ powder are indicated in Table 2. It was found that the

crystallographic properties obtained for the $CoAl_2O_4$ powder are in good agreement with the reported data[26].

***Table 2**: Crystallographic parameters for the $CoAl_2O_4$ powder.*

| S. No. | Properties | Standard XRD data for $CoAl_2O_4$ powder[25] | XRD data of $CoAl_2O_4$ powder with urea | XRD data of $CoAl_2O_4$ powder with glycine |
|---|---|---|---|---|
| 1. | Crystal structure | Cubic | Cubic | Cubic |
| 2. | Unit cell parameter (Å) | a = 8.1066 | a = 8.1099 | a = 8.1040 |
| 3. | Unit cell volume ($Å^3$) | 532.741 | 533.392 | 532.229 |
| 4. | Theoretical density ($g/cm^3$) | 3.0934 | 3.0975 | 3.0905 |
| 5. | Crystallite size (nm) | – | 20.89 | 16.66 |

The bulk and tap density values of $CoAl_2O_4$ powder were measured as described in literature[27] and the data is presented in Table 3. The density values are also in accordance with the reported values[26]. From the density data, it was found that the calcined particles were porous and fine.

The particle size distribution curves of $CoAl_2O_4$ powder prepared with urea and glycine as fuel are indicated in Figures 3 and 4. The frequency percentage is on the left hand side of the plot indicated by the line. The % on the right hand side of the plot corresponds to the particle distribution (histogram) indicated by the bars. The particle characteristics of $CoAl_2O_4$ from particle size analysis are presented in Table 3. In which, median particle diameter represents the particle diameter equal to 50 % of the cumulative distribution and mean particle diameter represents the arithmetically averaged value of the frequency distribution. From the curve (Fig. 3), it was found that the particle size of the powder was in the range of 0.087-88.58 μm. The median particle diameter was found to be 34.477 μm. From the curve (Fig. 4), it was found that the particle size of the powder was in between 0.150 - 1019.5 μm. The median particle diameter of the powder was found to be 523.634 μm. The larger size of particles found in particles prepared with glycine as fuel may be due to high temperature heat treatment[28]. The lower particle diameter found in the powder synthesized with urea as a fuel may be due to the large magnitude of heat of combustion in the precursors of $CoAl_2O_4$ during synthesis[29]. From the particle characteristics data, it was found that the $CoAl_2O_4$ powder prepared with urea as fuel is finer than the powder prepared with glycine as a fuel.

***Table 3**: Particulate properties for the $CoAl_2O_4$ powder.*

| S. No. | Sample | Bulk density ($g/cm^3$) | Tap density ($g/cm^3$) | Mean particle diameter (μm) | Median particle diameter (μm) |
|---|---|---|---|---|---|
| 1 | $CoAl_2O_4$ powder prepared with urea | 0.4358 | 0.6536 | 34.477 | 35.810 |
| 2 | $CoAl_2O_4$ powder prepared with glycine | 0.0923 | 0.1592 | 523.634 | 420.038 |

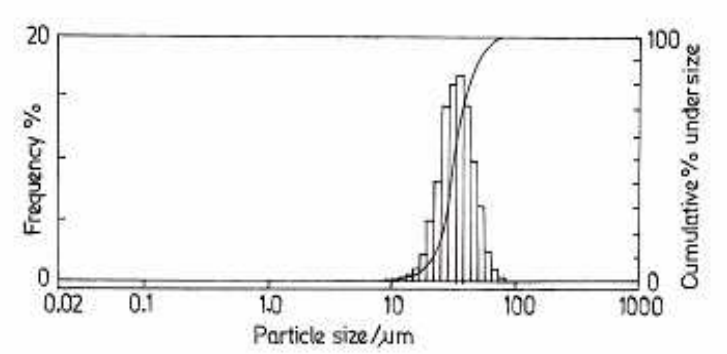


***Figure 3**: Particle size pattern for the $CoAl_2O_4$ powder using urea.*

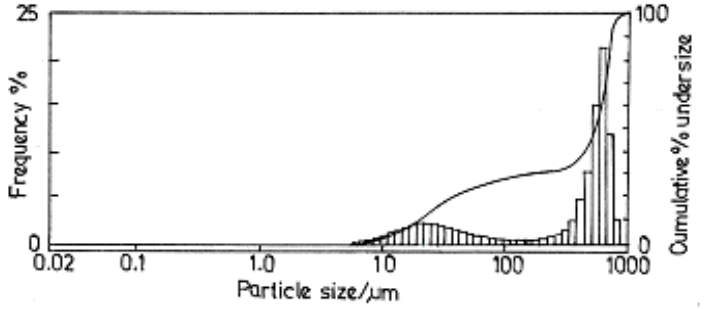


***Figure 4**: Particle size pattern for the $CoAl_2O_4$ powder glycine.*

The SEM micrographs of the calcined $CoAl_2O_4$ particles synthesized with urea and glycine as fuels are indicated in Figs 5 and 6, respectively. It was interesting to note that on calcination, the $CoAl_2O_4$ powder undergoes swelling and becoming more and more porous. The pore size of the powder is in the range 5–25 μm for both the samples. Also, the samples were quite agglomerated. It was reported that the flame temperature is responsible for agglomeration in ceramic oxides and the evolution of large amount gaseous products during combustion produces highly porous voluminous powders[30]. Figure 5 exhibits flake like morphology and the grain sizes found between 5-10 μm. Figure 6 shows the foamy like morphology with grain sizes between 10 – 300 μm. The larger grain sizes found in the powder synthesized with glycine as a fuel may be due to the agglomeration of particles at high temperature treatment, which was agreeable with the particle characteristics data.

## Conclusions

Combustion synthesis of $CoAl_2O_4$ spinel particles using urea and glycine as fuels is dealt with. The powder XRD data obtained on $CoAl_2O_4$ powder is in good agreement with the standard reported data. The particulate properties obtained on $CoAl_2O_4$ powder suggest that the as-formed materials are porous. The SEM photographs exhibit fluffy/foamy like morphology for the combustion derived products. Based on the structural and particle characteristics data, it is drawn that soft chemical synthesis with urea as a fuel may be used effectively to prepare $CoAl_2O_4$ spinels.

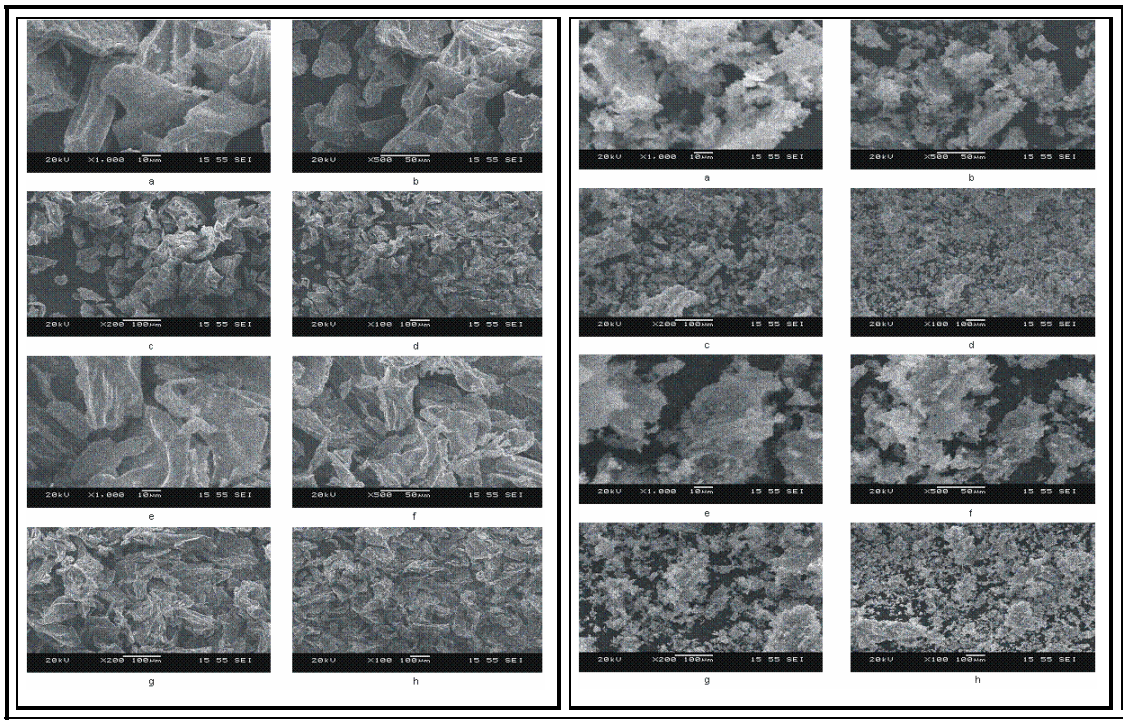

***Figure 5:*** *(a–h) SEM images on $CoAl_2O_4$ powder synthesized using urea.(a–1 magnification, b–500 magnification, c–200 magnification, d–100 magnification, e–1 magnification, f–500 magnification, g–200 magnification, h–100 magnification)*

***Figure 6:*** *(a–h) SEM images on $CoAl_2O_4$ powder synthesized using. (a–1 magnification, b–500 magnification, c–200 magnification, d–100 magnification, e–1 magnification, f–500 magnification, g–200 magnification, h–100 magnification)*

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