

The Powder Preparation of Blue Cobalt Aluminate at 210 °C Using the Malonate Method

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A powder, containing 80 percent of blue cobalt aluminate (CoAl₂O₄) crystallites, was synthesized at 210 °C using a (metal nitrate-malonic acid-ammonium hydroxide-ammonium nitrate) system. The optimal amount of concentrated ammonia water and initial decomposition temperature were determined for the blue CoAl₂O₄ crystallites preparation. Three CoAl₂O₄ precursor pastes, corresponding to the various amounts of concentrated ammonia water, were prepared by evaporating the initial solutions in an electric furnace fixed at 80 °C under a vacuum of 25 torr. The initial solution was used to dissolve the starting materials. The powder with the maximum content (80%) of blue CoAl₂O₄ crystallites was prepared when the prepared precursor was decomposed at 210 °C. The blue CoAl₂O₄ crystallite content in the prepared sample decreased with increasing initial decomposition temperature. For 0.2 mole of the Al³⁺ ion, the chemical compositions of the precursor corresponded to molar ratios of 0.4, 1.40, 2.56 and 2.00 for the Co²⁺ ion, malonic acid, ammonia and ammonium nitrate per mole of the Al³⁺ ion, respectively. The blue CoAl₂O₄ crystallite content in the sample decreased with the amount of ammonia deviated from the optimal value. The characteristics of the powders were examined using X-ray diffraction, optical microscopy, Fourier transformation infrared spectroscopy and the Brunauer-Emmett-Teller technique.

Key Words: Blue CoAl₂O₄, Powder, Malonic acid, Low temperature, Ammonium hydroxide

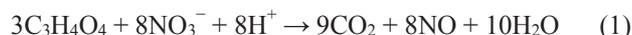
Introduction

Blue cobalt aluminate (CoAl₂O₄, CAO) plays an important role in many fields such as catalysts,^{1,2} sensors³ and pigments.⁴ A variety of techniques are used to prepare blue CAO powder.⁵⁻⁹ A combustion method can be used to produce mixed oxides such as blue CAO at low temperatures by burning fuel with the aid of the combustion heat. The parameters associated with this combustion method include the type of fuel, the fuel to oxidizer ratio, the ignition temperature and water content of the precursor mixture, *etc.* This process relies on the intimate blending of the constituents of a suitable fuel (e.g., citric acid, urea, glycine, *etc.*) in an aqueous medium and the exothermic redox reaction between the fuel and an oxidizer (i.e., nitrates). In this study, blue CAO was synthesized at a low temperature of 210 °C using the combustion technique with malonic acid as the fuel.

The choice of fuel is important in the preparation of mixed oxides at low temperature. Recently, Ianoş *et al.*¹⁰ reported that magnesium aluminate (MgAl₂O₄) was prepared at 300 °C using a mixture of fuels, urea and β-alanine. At the same temperature, however, an amorphous powder was prepared from the precursor of the individual fuel, urea or β-alanine. The fuel that is used to prepare mixed oxides at low temperature must be oxidized at a low temperature by an oxidant and immediately combusted once it decomposes at the decomposition temperature, so that the combustion heat increases the temperature of the system above the temperature used to prepare the mixed oxides.

Malonic acid (HOOCCH₂COOH) can be used as a fuel in the

preparation of mixed oxides at low temperature, because it oxidizes at below 50 °C in the acidic medium.¹¹⁻¹² However, these chemical properties of malonic acid negatively affect the preparation of mixed oxides. Carbonate salt is produced if nitrate (NO₃⁻) anions oxidize malonic acid while preparing the precursor of mixed oxide from the initial solution. (The initial solution is the aqueous solution that includes all of the starting materials.) Malonic acid reduces the nitrate anion to nitrogen monoxide (NO) or nitrogen dioxide (NO₂) in the following chemical equation:



The oxidation reactions in Equations (1) and (2) reduce the negative charges in the system. The deficient negative charges in the system are compensated by the hydrogen-carbonate (HC-O₃⁻) and/or carbonate (CO₃²⁻) anions depending on the amount of malonic acid used. The decomposition of the carbonate anion is an intra-molecular reaction. Therefore, the carbonate salt in the prepared precursor produces the parent oxide after it is decomposed. As a result, the oxidation should be controlled by the precursor preparation process.

An experimental method must be used to form an insoluble malonate salt in the initial solution in order to inhibit the oxidation of malonic acid or its derivatives with the nitrate anion. In this study, concentrated ammonia water was used in the pre-

cursors to form the malonate salt. Three precursors of blue CAO were prepared with various amounts of concentrated ammonia water using the (metal nitrate-malonic acid-ammonium hydroxide-ammonium nitrate) system. The prepared precursors were decomposed at 210 °C in air, and the powders that were obtained at 210 °C were heated at different temperatures. The characteristics of the prepared powders were investigated using X-ray diffraction (XRD), optical microscopy, Fourier transformation infrared (FTIR) spectroscopy and the Brunauer-Emmett-Teller (BET) technique.

Experimental

Preparation of sample powders. Basic cobalt carbonate (Samchun, Korea), aluminum nitrate nonahydrate (Daejung, Korea), malonic acid (Junsei, Japan), concentrated ammonia water and ammonium nitrate (Duksan, Korea) were used as the starting materials. A solution of basic cobalt carbonate and aluminum nitrate was prepared at 60 °C, and ammonium nitrate was added to the mixture. Then malonic acid was dissolved in concentrated ammonia water. The two solutions were mixed together and stirred at room temperature under a vacuum of 25 torr until a precipitate formed in the initial solution. Any excess water was removed in an electric furnace at 80 °C and 25 torr until the solution formed a paste. The precursor paste was decomposed at 210 °C in air while the temperature of the electrical furnace was raised by the combustion heat. Although the heating time was 2 ~ 3 hours, the combustion occurred over a period of about 10 seconds, and the powder was red-heated in a stainless-steel bottle.

In this experiment, 0.2 mole of aluminum nitrate nonahydrate, 0.08 mole of Co^{2+} ion, 0.28 mole of malonic acid, and 0.4 mole of ammonium nitrate were used. Ammonium nitrate was used in order to replenish the deficiencies in the nitrate anions. The predetermined ratio of malonic acid to nitrate anions was 0.28. The concentration of concentrated ammonia water was 27.8%, and 31, 35 and 39 mL of ammonia water were used for the three precursors. Hereafter, the precursor prepared with 35 mL of ammonia water will be referred to as 35-precursor.

The 35-precursor was decomposed at 260 and 310 °C in order to determine the effect of the decomposition temperature. The powders obtained at 210 °C were heated to 700, 900, 1100, 1300 and 1400 °C in air at a heating rate of 1.67 °C/min. The powders were heated at the temperatures for 12 hours.

Characterization of samples. The powders were examined by X-ray powder diffraction using a MAC Science MXP³ system equipped with a copper target (0.15418 nm) and an X-ray tube voltage and current of 40 kV and 10 mA, respectively. The diffraction patterns were recorded in the range of 25 ~ 70° with a step-size of $2\theta = 0.04^\circ$ at 0.5 sec/step. The area and intensity of the diffraction peak were obtained using the software that was included with the diffractometer. The mass was assumed to be constant in order to ignore the mass effect.

The FTIR spectra were obtained in air at room temperature over a range 400 - 1000 cm^{-1} using KBr disks on a JASCO FT/IR 5300 spectrometer with a resolution of 2 cm^{-1} . The surface areas of the samples were obtained using the BET technique on a Quantachrome Autosorb-1 after powders were degassed at

250 °C for 6 h. The optical images (Olympus BX60M) of the samples were recorded using the reflectance technique in order to identify the phase of the impurity oxides, black Co_3O_4 and green Co_2AlO_4 .

Results and Discussion

The effect of the used amount of concentrated ammonia water. Figure 1 shows the XRD patterns of the samples obtained at 210 °C from three precursors prepared with various amounts of ammonia water. The three patterns contained the characteristic peaks of the spinel structure. The blue CAO crystallites in the samples was of interest but the un-reacted impurity oxides, black Co_3O_4 (JCPDS 44-0160) and green Co_2AlO_4 (JCPDS 38-0814), have spinel structures. The presence of these impurity oxides in the samples was identified using optical microscopy in Fig. 2. The optical images had black spots in the blue background, with the sample prepared from the 35-precursor having the smallest population of black spots. Therefore, the sample prepared from the 35-precursor contained more blue CAO crystallites than the samples prepared from the 31- and 39-precursors. This result supported the analysis of the integrated area of the (311) peak and the FTIR spectroscopy.

Figure 3 shows the integrated areas of the (311) peak (the maximum peak in the spinel structure) in Fig. 1, and the sample prepared from the 35-precursor had the largest peak area. In the FTIR spectrum of blue CAO, two absorption bands were observed at around 510 and 550 cm^{-1} for the CoO_4 tetrahedra and the band at 666 cm^{-1} was caused by the AlO_6 octahedra.¹³ From Fig. 4, the two bands caused by the CoO_4 tetrahedra were separated in the FTIR spectrum for the 35-precursor, whereas the two bands overlapped in the spectra for the 31- and 39-precursors. The optimal molar ratio of ammonia to Al^{3+} ion was 2.56 as 35 mL of 27.8% ammonia water (0.512 mole) was used.

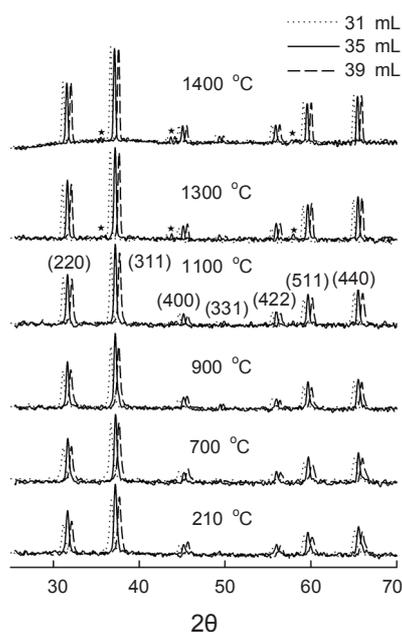


Figure 1. XRD patterns of the samples prepared from the three precursors.

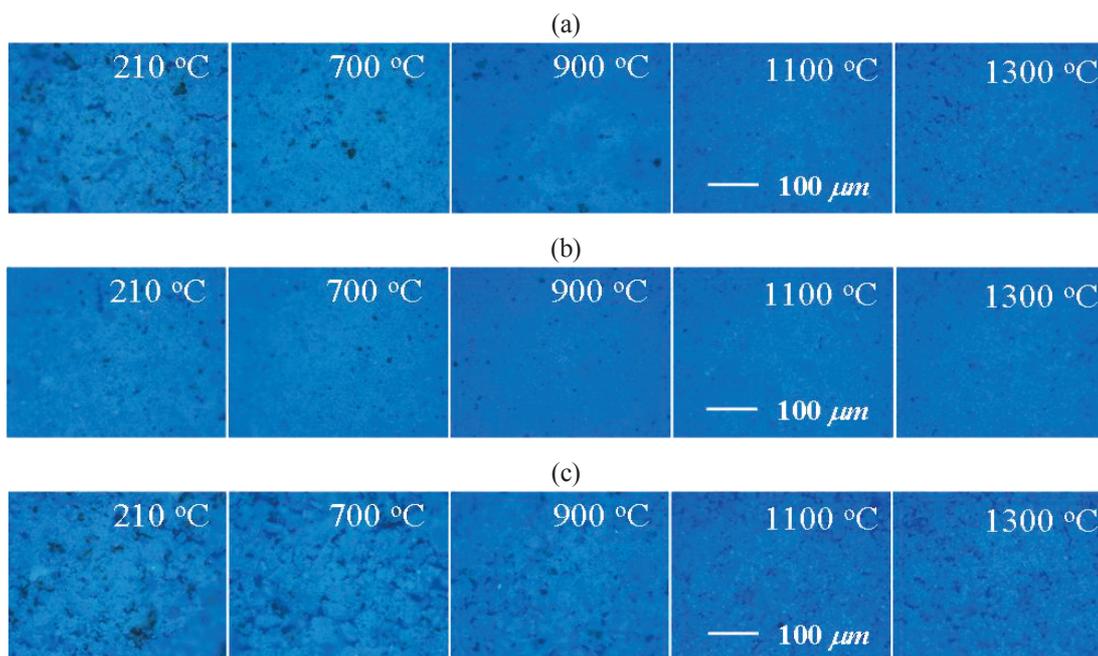


Figure 2. Optical images of the samples prepared from the (a) 31-, (b) 35-, and 39-precursors.

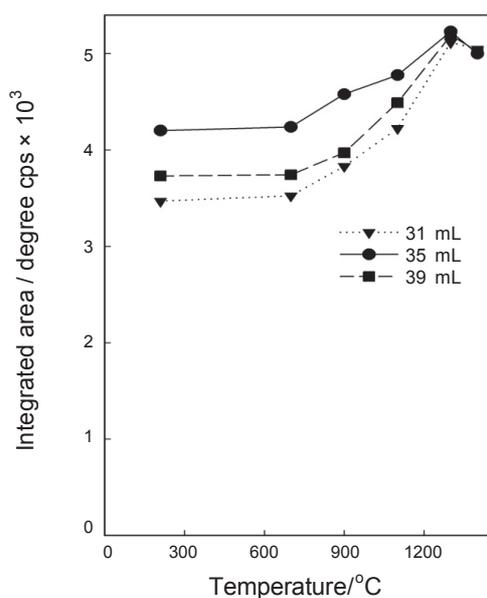


Figure 3. Integrated areas of the (311) peak for the samples prepared at the given temperatures.

Additional studies may be required to investigate the reasoning behind these results.

The effect of the sintering temperature on the samples obtained at 210 °C. Figure 1 shows the XRD patterns of the samples prepared at various temperatures. The XRD patterns of the samples obtained at 1300 and 1400 °C exhibited (104), (113) and (116) peaks because of the α -Al₂O₃ phase in addition to the peaks for the blue CAO phase. The area ratio of the (113) peak of α -Al₂O₃ to the (311) peak of blue CAO was calculated in order to estimate the fraction of α -Al₂O₃, with values of 0.0404 and 0.0544 at 1300 and 1400 °C, respectively. Therefore, the α -

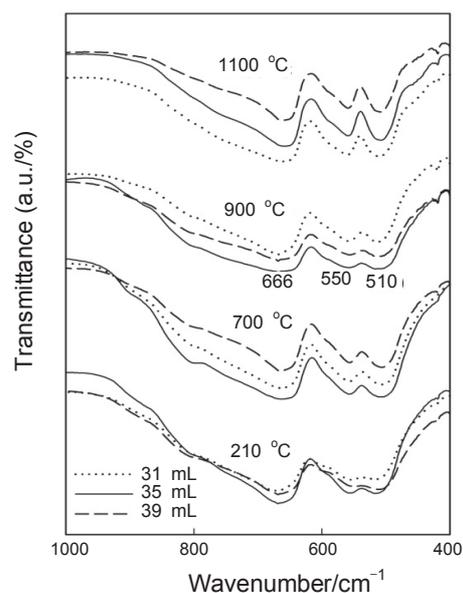


Figure 4. FTIR spectra of the samples prepared at the given temperatures.

Al₂O₃ crystallite content was greater at 1400 °C than 1300 °C.

Black spots were not observed in the optical images of the samples prepared at 1100 °C. (Fig. 2) From Fig. 4, the two bands caused by the CoO₄ tetrahedra were clearly separated at 1100 °C. In Fig. 3, the integrated areas for the samples prepared at 1300 °C were larger than at 1100 °C, and had the maximum value. It was considered that the number of blue CAO crystallites formed increase from 1100 to 1300 °C because the amorphous blue CAO that was dissolved in the amorphous aluminum oxide crystallized.¹⁴ The (311) peak areas decreased from 1300 to 1400 °C, suggesting that the amorphous aluminum oxide was converted

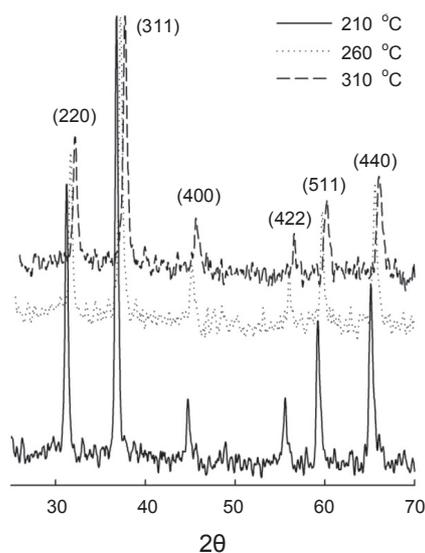


Figure 5. XRD patterns of the samples obtained by decomposing the 35-precursor at 260 and 310 °C.



Figure 6. Optical images of the samples obtained by decomposing the 35-precursor at 260 and 310 °C.

to α - Al_2O_3 crystallites after the blue CAO crystallites were completely formed. The α - Al_2O_3 phase of polymorphic aluminum oxides is known to form at temperatures above 1000 °C.¹⁵ The blue CAO crystallite contents in the samples prepared at 210 °C could be determined using the maximum value of the (311) peak. The sample concentrations obtained from the 31-, 35- and 39-precursors were 66, 80 and 71%, respectively.

The effect of the initial decomposition temperature. Figure 5 shows the XRD patterns of the samples obtained by decomposing the 35-precursor in the furnace at 260 and 310 °C. The XRD patterns contained the characteristic peaks of the spinel structure, similar to the sample prepared at 210 °C. However, the (311) peak intensity decreases with increasing initial decomposition temperature. In other words, the blue CAO crystallite concentration decreased at higher decomposition temperatures. Figure 6 shows the optical images of the samples in Fig. 5. The number of black spots increased at higher initial decomposition temperatures, and white lumps were observed in the optical image for the sample obtained at 310 °C. These white lumps must have represented amorphous aluminum oxide, because most of salts were decomposed by the combustion heat. Therefore, the salts that were in the prepared precursor were not simultaneously decomposed, leading to the decreased blue CAO crystallite content at higher decomposition temperatures. As a result, the driving force of the blue CAO crystallite formation was the combustion heat because of the simultaneous decomposition of the salts that were present in the precursor. The opti-

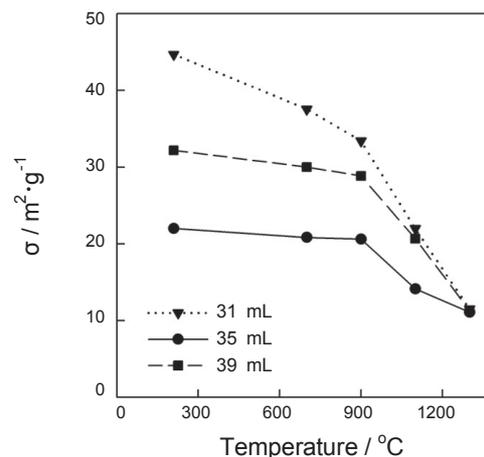


Figure 7. Specific surface areas (σ) of the samples prepared at the given temperatures.

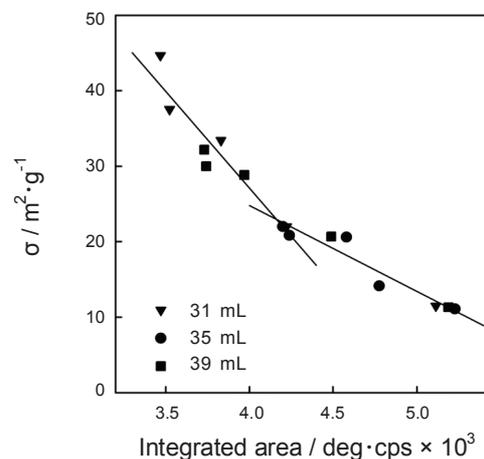


Figure 8. Plot of the specific surface areas (σ) versus the integrated (311) peak areas for the samples prepared at the given temperatures.

mal decomposition temperature of the prepared precursors was 210 °C, which was lower than the temperature (300 °C) of the precursors that were prepared using the (nitrate-citric acid-ammonium hydroxide) system.¹⁶

The relation between the specific surface area and the content of blue CAO crystallites. Figure 7 shows the specific surface areas of the prepared samples. In spite of the prepared precursors combusting in about 10 seconds, as mentioned in the experimental section, the sample prepared at 210 °C using the 35-precursor had a small specific surface area ($\sigma = 22.0 \text{ m}^2 \cdot \text{g}^{-1}$). In general, the powder prepared at lower temperatures tended to have a large σ . Here, the magnitude of σ was expected to be related to the content of the CAO crystallites. Figure 8 shows the plot of σ with respect to the (311) peak area. In this figure, the magnitude of σ depended on the blue CAO crystallite content in the prepared sample, and two different slopes were observed.

The amount of amorphous aluminum oxide decreased as the blue CAO crystallites formed. However, problems occurred depending on which phase of the Al_2O_3 polymorphs was present in the prepared samples. The γ - Al_2O_3 particles were nano-siz-

ed.¹⁷ Assuming that the γ -Al₂O₃ phase was present, the dependencies of σ' can be interpreted with respect to the blue CAO crystallite content.

In the samples containing small amounts of the blue CAO crystallites, the magnitude of σ mostly determined the amount of amorphous Al₂O₃, and σ' rapidly decreased as the blue CAO crystallites formed. On the contrary, in the samples including large amounts of the blue CAO crystallites, the magnitude of σ was related to the particle sizes of blue CAO and amorphous Al₂O₃. Amorphous Al₂O₃ was not present in the samples prepared at 1300 °C. The average size of the blue CAO crystallites was 123 nm at 1300 °C and was calculated from the σ value and the theoretical density (4.416 g·cm⁻³) of blue CAO. Therefore, the σ' of the samples that contained small amounts of amorphous Al₂O₃ slowly decreased with the formation of the blue CAO crystallites. As a result, Fig. 8 exhibited an inflection point.

Conclusion

Blue cobalt aluminate (CAO) was prepared at 210 °C using the (metal nitrate-malonic acid-ammonium hydroxide-ammonium nitrate) system. The driving force for the formation of the blue CAO crystallites was the combustion heat of the malonate and nitrate anions. The optimal amount of concentrated ammonia water and the optimal initial decomposition temperature of the prepared precursor were determined among the parameters that affected the combustion. When 0.2 mole of Al³⁺ ion was used, the molar ratios of the Co²⁺ ion, malonic acid, ammonia and ammonium nitrate to Al³⁺ ion were 0.4, 1.40, 2.56 and 2.00, respectively. The powder obtained at 210 °C from this pre-

cursor included 80% of blue CAO crystallites. The average size of blue CAO crystallites was 123 nm.

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