The Preparation of Blue CoAl₂O₄ Powders by the Malonate Method: The Effect of the Amount of Malonic Acid Used, the Formation Pathway of CoAl₂O₄ Crystallites and the Characteristics of the Prepared Powders

Gong Yeol Lee, Kwang Hyun Ryu,† Hong Gun Kim,‡ and Yoo Young Kim§,*

Korea Testing and Research Institute, Jeonju, Jeonbuk 561-481, Korea
†EN Chem, Goyang, Gyeonggi 410-314, Korea
‡Department of Mechanical and Automotive Engineering, Jeonju University, Jeonju, Jeonbuk 560-759, Korea
§Department of Nano and Advanced Materials Engineering, Jeonju University, Jeonju, Jeonbuk 560-759, Korea
*E-mail: yooynam@ktristek.or.kr
Received July 10, 2008, Accepted December 19, 2008

A pathway for the formation of normal CoAl₂O₄ particles is suggested. The optimal amount of malonic acid was determined, and the characteristics of the obtained powders were investigated. Normal CoAl₂O₄ powders were prepared using solutions of malonic acid and metal nitrates. X-ray diffraction, Brunauer-Emmett-Teller (BET) and scanning electron microscope (SEM) measurements, as well as Fourier transform infrared (FTIR) and ultraviolet/visible (UV-Vis) spectroscopy were carried out. Normal CoAl₂O₄ crystallites were formed by a solid state reaction between Co₂AlO₄ and amorphous aluminum oxide. The optimal molar ratio of malonic acid to the nitrate anions present in the initial solution was found to be 0.30–0.35. The particles were composed of agglomerates of primary particles. The primary particles were 40 nm in size. This size was relatively constant regardless of the preparation temperature. However, the size of the agglomerated particles increased to 220 nm with increasing temperature.

Key Words: Normal CoAl₂O₄, Powder, Preparation, Malonic acid

Introduction

Normal cobalt aluminate (CoAl₂O₄) with a blue coloration plays an important role in many fields such as catalysts,¹,² sensors³ and pigments.⁴ A variety of techniques are used to prepare CoAl₂O₄.⁵ The formation of blue CoAl₂O₄ is a solid state reaction between Co₂AlO₄ and amorphous aluminum oxide. The oxide phases present in the powder obtained at temperatures below 800 °C are cobalt oxide (CoO₂), cobalt cobalto-aluminate (Co₂AlO₄) and/or aluminum oxide (Al₂O₃). CoAl₂O₄ crystallites are formed by a solid state reaction between Co₂AlO₄ and Al₂O₃, and/or between Co₃O₄ and Al₂O₃. Therefore, the formation of Co₂AlO₄ and Co₃O₄ with the combustion of a solidified precursor leads to an increase in the preparation temperature of blue CoAl₂O₄.

For the preparation of blue CoAl₂O₄ by the combustion technique, the combustion heat should be above 800 °C, as mentioned above. Cobalt malonate and aluminum nitrate decompose completely at 360°C and 500 °C, respectively. As the decomposition of the malonate anion in air is exothermic, the heat emitted by the combustion of the malonate might contribute to the formation of blue CoAl₂O₄. Therefore, it is essential to determine the formation pathway of CoAl₂O₄ in order to prepare the CoAl₂O₄ crystallites at lower temperatures using the malonate method.

In this study, powder X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) and scanning electron microscopy (SEM), and Fourier transform infrared (FTIR) and ultraviolet/visible (UV-Vis) spectroscopy were used to determine the optimal amount of malonic acid for the preparation of normal CoAl₂O₄ powder. In addition, the formation pathway of the CoAl₂O₄ crystallites was suggested, and the characteristics of the obtained powders were investigated.

Experimental

Preparation of sample powders. The N-CAO samples were prepared as follows. 0.05 moles of cobalt nitrate (Junsei, Japan) and a predetermined amount of malonic acid (HOOCCH₂
COOH; Junsei, Japan) according to the R value were dissolved in a solution containing 0.1 moles of aluminum nitrate (Samchun, Korea) in 20 g of distilled water. R is the malonic acid to nitrate molar ratio and ranged from 0.25 to 0.40. The solution was heated for 4 h at 350 °C and the obtained powder was heated to 700 °C. The resulting powder was ball-milled for 12 h with distilled water at room temperature and filtered. The filtered powder was dried for 24 h at 100 °C. The dried powder was roughly ground and heated for 12 and 4 h at 1000 and 1250 °C, respectively.

The C-CAO samples were obtained from the solutions used to dissolve a stoichiometric amount of basic cobalt carbonate (Samchun, Korea) and a predetermined amount of malonic acid in the aluminum nitrate solution. In order to eliminate carbon dioxide, the solutions containing the three compounds were left to stand for 24 h at room temperature. The forward processes were the same as the abovementioned processes.

**Characterization of samples.** The obtained samples were examined by X-ray powder diffraction using a MAC Science MXP³ system equipped with a copper target (0.15418 nm). X-ray tube voltage and current were 40 kV and 10 mA, respectively. The diffraction patterns were recorded in the 2θ = 28–70° range with a step-size of 2θ = 0.05° and 0.5 sec/step. The area and intensity of the diffraction peak, which was recorded with a step-size of 2θ = 0.006° and 0.5 sec/step, were obtained using the software included with the diffractometer. A constant mass was used in order to ignore the mass effect.

The FTIR spectra were obtained in air at room temperature over the range 400-2100 cm⁻¹ using KBr disks on a JASCO FT/IR 5300 spectrometer. The resolution was 2 cm⁻¹. The UV-VIS spectra (Varian Cary 500 Scan spectrophotometer) were acquired using the diffuse reflectance technique in order to examine the local structure of Co²⁺ cation.

The surface areas of the samples were obtained using the BET technique on a Quantachrome Autosorb-1. The samples were degassed at 250 °C for 6 h. The SEM images were recorded on a Jeol JSM-840A instrument after coating the samples with platinum.

**Results and Discussion**

**Determination of the suitable amount of malonic acid.** Figure 1 shows the XRD patterns of the N-CAO samples obtained at 1250 °C. Although each pattern shows the characteristic peaks of the spinel structure, it cannot be concluded they are from the normal CoAl₂O₄ phase. This is because Co₃O₄ and Co₂AlO₄ have a spinel structure. Fortunately, the lattice parameter of CoAl₂O₄ (0.8104 nm, JCPDS 44-0160) is larger than those of Co₃O₄ (0.8084 nm, JCPDS 42-1476) and Co₂AlO₄ (0.8086 nm, JCPDS 38-0814). Based on the difference in lattice parameter between CoAl₂O₄ and Co₂AlO₄, the 2θ difference in the (440) peak between two compounds was 0.16° 2θ. The two peaks could be resolved (Fig. 2). The (440) peak due to the Co₃O₄ or Co₂AlO₄ phase was observed in the diffraction pattern of the N-CAO sample with R = 0.40. However, although not indicated in the patterns of the other samples, the contents of normal CoAl₂O₄ crystallites were different.

In general, the intensity and area of a spectroscopic peak reflects the concentration of the substance responsible. Figure 3 shows the (311) peaks, the maximum peaks, of the N-CAO samples obtained at 1250 °C. The (311) peak of the N-CAO
The Preparation of Blue CoAl₂O₄ Powders by the Malonate Method


The sample with \( R = 0.30 \) showed the highest intensity and widest area. The ratios of the intensities and areas of the other peaks were calculated based on the intensity and area of this peak. Figure 4 shows the calculation results. The N-CAO and the C-CAO series have a maximum at \( R = 0.30 \) and 0.35, respectively. This suggests that the optimal amount of malonic acid corresponds to a \( R \) value ranging from 0.30 to 0.35, and also suggests that the presence of an amorphous phase in all of the samples except the N-CAO sample obtained at 1250 °C with \( R = 0.30 \). Identification of the amorphous substance will help determine the pathway for the formation of CoAl₂O₄.

**Formation pathway of CoAl₂O₄.** Figure 5 shows the XRD patterns of the N-CAO samples obtained at 1250, 1000 and 700 °C from a solution with \( R = 0.30 \). The three patterns contain the characteristic peaks of the spinel structure. However, the spectroscopic characteristics of the N-CAO sample obtained at 700 °C were clearly different from those of the other two samples.

Figures 6 and 7 show the FTIR and UV-Vis reflectance spectra of the above three samples, respectively. The FTIR spectra in Figure 6(a) and (b) show the characteristic bands due to normal CoAl₂O₄ at below 800 cm⁻¹.⁶,⁸ The absorption band at 666 cm⁻¹ was assigned to the Al-O stretching vibration of the AlO₆ octahedra and the bands at 511 and 556 cm⁻¹ were attributed to the Co-O stretching vibration of the CoO₆ tetra-

hedra.¹² However, the characteristic bands for CoAl₂O₄ were not observed in the FTIR spectrum of Fig 6(c).

Figure 7(a) and (b) show three absorption bands in the UV-Vis reflectance spectra due to spin-allowed transitions of Co²⁺ ions in tetrahedral or octahedral coordination⁶ at 500–700 nm, whereas the spectrum in Fig. 7(c) does not show these bands. The major phase in the sample obtained at 1000 °C was normal CoAl₂O₄ whereas, from Fig. 5, the sample prepared at 700 °C contained the CoO₂ and/or Co₂Al₂O₄ crystallites as the major phase. Therefore, the amorphous material is a polymorph of aluminum oxide. The main problem is which compound the peaks in the diffraction pattern of the sample at 700 °C refer to.

The sample obtained at 700 °C had a slightly dark green color. The coloration of a mixture of black Co₃O₄ with white Al₂O₃ is grey. If the sample at 700 °C contains a mixture of Co₃O₄ and Al₂O₃, the content of the normal CoAl₂O₄ crystallites in a sample obtained from it at 1000 °C would be very small. The CoAl₂O₄ crystallites by a solid state reaction of the parent oxides are produced at above 1200 °C. As a result, the
CoAl$_2$O$_4$ crystallites in this study were formed by a solid state reaction from a mixture of Co$_2$AlO$_4$ and amorphous Al$_2$O$_3$ at high preparation temperature.

**Effect of the amount of malonic acid used on the obtained powder.** CoAl$_2$O$_4$ crystallites are generated from a mixture of Co$_2$AlO$_4$ crystallites and amorphous Al$_2$O$_3$, as mentioned above. One of two Co ions in a single formular unit of Co$_2$AlO$_4$ has a trivalent state. This Co ion needs to be reduced to the divalent state to form normal CoAl$_2$O$_4$. The combustion of malonic acid becomes more reductive with increasing amounts. Nevertheless, the change of the content of CoAl$_2$O$_4$ crystallites in the final product does not follow this trend. (Refer to Fig. 4.)

An increase in the amount of malonic acid leads to the formation of its Co salts. The produced salts will be isolated in a solidified precursor. The isolated salts form Co$_3$O$_4$ crystallites by the intramolecular decomposition. Therefore, the normal CoAl$_2$O$_4$ powder prepared at lower temperature contains the parent oxides as the impurity. This claim is supported by the results for the C-CAO samples from Fig. 4. Most of malonic acid added to the initial solutions of the C-CAO series was present as malonate and hydrogenmalonate anions. The content of CoAl$_2$O$_4$ crystallites in the N-CAO sample with $R = 0.30$ was smaller than that in the C-CAO sample with $R = 0.35$.

On the other hand, a decrease in the amount of malonic acid promotes a more oxidative atmosphere. As a matter of course, the formation of Co$_3$O$_4$ crystallites is easier. Therefore, there is an optimal $R$ value; 0.30~0.35. This is because the nitrate (NO$_3^-$) anion reduces to nitrogen oxide (NO) or nitrogen dioxide (NO$_2$). All the NO$_3^-$ anions present in the initial solution are reduced completely to nitrogen oxide or nitrogen dioxide at a malonic acid to NO$_3^-$ molar ratio of 0.375 or 0.125 according to the respective equations below:

$$3C_3H_4O_4 + 8NO_3^- + 8H^+ \rightarrow 9CO_2 + 8NO + 10H_2O$$  

$$C_3H_4O_4 + 8NO_3^- + 8H^+ \rightarrow 3CO_2 + 8NO_2 + 6H_2O$$

Under the condition that $R > 0.375$, malonic acid may lead to incomplete combustion whereas the parent oxides will remain in the product when $R < 0.125$. The nitrate salts produce the oxides. The maximum and minimum limits of $R$ in this study were determined to be $< 0.375$ and $> 0.125$, respectively. From experimental observations, a brown NO$_2$ gas evolved after heating the initial solutions to 350 °C.

**Particle size of samples obtained.** The specific surface areas of the N-CAO samples with $R = 0.30$ at 1000 and 1250 °C are 22.8 and 6.27 m$^2$/g. Under the assumption that the particle shape is cubic, the average particle size was calculated to be 59.6 and 217 nm, respectively, using the surface area measured and the theoretical density (4.416 g/cm$^3$) of CoAl$_2$O$_4$.

In addition, the average particle size was estimated using the Scherrer equation from the full width at half maximum (FWHM) of the diffracted peak as follows:

$$D_{hkl} = \frac{K \lambda}{\beta_{hkl} \cos \theta}$$  

where $K$ is a constant (normally equal to 0.89), $\lambda$ is the wavelength of the incident X-ray radiation (0.15418 nm in this study) and $\beta_{hkl}$ is the FWHM in radians. The value, $\theta$ is half of 20, the position of the reflection in radians, from which the $\beta_{hkl}$ is taken. The FWHM values of the (311) peak for the two samples was 0.21°. The average particle size estimated from this FWHM value by equation (3) was 39.5 nm. This size is smaller than that determined using the BET technique. This suggests that growth occurs through aggregation between the primary particles proceeds with increasing preparation temperature rather than by crystal growth. Figure 8 indicated no grain growth had occurred.

**Conclusions**

Normal CoAl$_2$O$_4$ crystallites were produced by a solid state reaction of Co$_2$AlO$_4$ crystallites and amorphous Al$_2$O$_3$. The amount of malonic acid used was found to influence the content of CoAl$_2$O$_4$ crystallites in the final product. The optimal malonic acid to nitrate molar ratio in the initial solution was found to be 0.30~0.35.

The particles of the sample powders consisted of agglomerates of primary particles. The size of the primary particles was approximately 40 nm and was constant regardless of the preparation temperature. The average size of the agglomerated particles obtained at 1000 °C and 1250 °C was 60 and 220 nm, respectively. Therefore, particle growth proceeded by agglomeration with a rate that increases with increasing temperature rather than by crystal growth.

![Figure 7](image-url)  
Figure 7. UV-Vis reflectance spectra of the N-CAO samples obtained at 1250 (a), 1000 (b) and 700 (c) °C from the solution with $R = 0.30$. The band at 497 nm is due to the spin-forbidden transition of Co$^{2+}$ ion.

![Figure 8](image-url)  
Figure 8. SEM images of the samples obtained at 1000 (a) and 1250 (b) °C from the solution with $R = 0.30$. 
The Preparation of Blue CoAl$_2$O$_4$ Powders by the Malonate Method

References

1. Liotta, L. F.; Pantaleo, G.; Di Carlo, G.; Marci, G.; Deganello, G. 
   **2001**, *207*, 247.
3. Vijaya, J. J.; Kennedy, L. J.; Sekaran, G.; Jeyaraj, B.; Nagaraja, 
8. Ouahdi, N.; Guillemot, S.; Demai, J. J.; Durand, B.; Er Rakho, 