

Research Article

Formation of CoAl_2O_4 Nanoparticles via Low-Temperature Solid-State Reaction of Fine Gibbsite and Cobalt Precursor

Natpakan Srisawad,¹ Wasu Chaitree,¹ Okorn Mekasuwandumrong,²
Piyasan Praserttham,¹ and Joongjai Panpranot¹

¹Department of Chemical Engineering, Faculty of Engineering, Center of Excellence on Catalysis and Catalytic Reaction Engineering, Chulalongkorn University, Bangkok 10330, Thailand

²Department of Chemical Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, Nakhon Pathom 73000, Thailand

Correspondence should be addressed to Joongjai Panpranot, joongjai.p@chula.ac.th

Received 13 July 2012; Revised 14 August 2012; Accepted 16 August 2012

Academic Editor: Alireza Khataee

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Nanocrystalline cobalt aluminate (CoAl_2O_4) was synthesized by the solid-state reaction method with cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) as the source of Co and gibbsite ($\text{Al}(\text{OH})_3$) as the source of Al, respectively. The effects of particle size of the starting fine gibbsite (0.6 and 13 μm) and calcination temperatures (450, 550, and 650°C) on the properties of CoAl_2O_4 were investigated by means of X-ray diffraction (XRD), thermogravimetry analysis and differential thermal analysis (TG/DTA), X-ray photoelectron spectroscopy (XPS), UV-visible absorption spectroscopy (UV-Vis), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Increasing of calcination temperature promoted the insertion amounts of Co^{2+} in alumina matrix in CoAl_2O_4 structure, which resulted in the brighter blue particles and increasing of UV spectra band. The lowest temperature for the formation of nanocrystalline CoAl_2O_4 particles was 550°C for the solid-state reaction of cobalt chloride and 0.6 μm fine gibbsite.

1. Introduction

Cobalt aluminate is a binary oxide consisting of cobalt and aluminium oxides. It is a thermally and chemically stable pigment of intense blue color and is usually synthesized at high temperature by solid-state reaction between two oxide components [1, 2]. In the past decades, it has received attention due to its applications as inorganic ceramic blue pigment which is widely used for coloration of plastics, paint, fiber, paper, rubber, phosphor, glass, cement, glazes, ceramic bodies, and porcelain enamels [3–5]. Moreover, its unique optical properties lead to its extensive use as color filter for automotive lamps or pigment layer on luminescent materials in optical devices [6–8]. The coloring performance of cobalt pigments strongly depends on their thermal stability, chemical reactivity, and coordination of Co^{2+} ions [9]. Other applications of cobalt aluminate are an important material for heterogeneous catalysis such as selective catalytic reduction of NO_x with hydrocarbons [10] and carbon dioxide reforming of methane [11].

Cobalt aluminate can be synthesized by various routes such as polymerized complex [3], molten salt [4], polyol [8], low-temperature combustion [9], coprecipitation [7, 12], sol-gel [13–15], citrate-gel [16], metal-organic chemical vapor deposition (MOCVD) [17], EDTA chelating precursor [18], glycine chelated precursor [19], hydrothermal [20], polymer aerosol pyrolysis [21], and reverse micelle processes [22]. Nonetheless, the selection of preparation method is usually based upon the desired properties of the final materials [3]. The solid-state reaction of a mechanical mixture between gibbsite and cobalt precursor is interesting due to three main advantages approach. They (i) are simple, cheaper, and convenient, (ii) involve less solvent and reduce contamination, and (iii) give high yields of products [23]. The solid-state reactions involve four steps in a typical proceeding: diffusion, reaction, nucleation, and growth. Any chemical interaction between solids proceeds exclusively on the contact area between the particles [24].

In the present work, cobalt aluminate was synthesized by the solid-state reaction method with cobalt chloride

hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) as the source of Co and gibbsite ($\text{Al}(\text{OH})_3$) as the source of Al, respectively. The effects of particle size of gibbsite and calcination temperature on the formation of cobalt aluminate and their properties were investigated by means of X-ray diffraction (XRD), thermogravimetry analysis and differential thermal analysis (TG/DTA), X-ray photoelectron spectroscopy (XPS), UV-visible absorption spectroscopy (UV-Vis), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

2. Experimental

2.1. Preparation of CoAl_2O_4 . Fine gibbsite ($\text{Al}(\text{OH})_3$, Merck) and cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, Fluka) were used as starting materials. The starting fine gibbsite has an average particle size of $13 \mu\text{m}$ and is denoted as FG-13 μm . After milling of 100 g of fine gibbsite in an attrition mill for 24 h, the particle size of the fine gibbsite was reduced to $0.6 \mu\text{m}$ and is denoted as FG-0.6 μm [25]. The solid-state reaction between fine gibbsite and cobalt chloride took place at 450, 550, and 650°C with a Co : Al molar ratio 1 : 6. Firstly, a certain amount of fine gibbsite and cobalt chloride hexahydrate was mixed in an agate mortar. Secondly, the mixed materials were dried in oven at 110°C overnight. Finally, the mixtures were calcined in a tube furnace in an air flow (95 mL/min) by heating to a desired temperature (450, 550, and 650°C) at a rate of $10^\circ\text{C}/\text{min}$ and held at that temperature for 5 h. Then, the mixed materials were cooled down to room temperature in N_2 (75 mL/min).

2.2. Characterization. Particle size distribution was measured using a laser diffraction-based size analyzer (Malvern Mastersizer, reflective index 1.57). All the samples were done on deionized water as dispersant. Dispersion and deagglomeration of particles were ensured by ultrasonic treatment before measurement. XRD was performed to determine the bulk phase of particles by SIEMENS D 5000 X-ray diffractometer connected with a computer with Diffract ZT version 3.3 programs for full control of the XRD analyzer. The experiments were carried out by using $\text{CuK}\alpha$ radiation with Ni filter in the 2θ range of 10–80 degrees resolution 0.04° . The crystallite size was estimated from line broadening according to the Scherrer's equation and α -alumina ($\alpha\text{-Al}_2\text{O}_3$) as an external standard. The decomposition of cobalt chloride and fine gibbsite and CoAl_2O_4 formation was studied by TG/DTA using an SDT Analyzer Model Q600 from TA Instruments, USA, from room temperature to 1000°C at a heating rate of $10^\circ\text{C}/\text{min}$ in air. The chemical state of Co and surface elemental composition were determined by XPS analysis using an AMICUS spectrometer equipped with an $\text{MgK}\alpha$ X-ray radiation. For a typical analysis, the source was operated at voltage of 15 kV and current of 12 mA. The pressure in the analysis chamber was less than 10^{-5} Pa. The AMICUS system is computer controlled using the AMICUS "VISION 2" software. The optical properties of CoAl_2O_4 particles were studied by UV-Vis analysis using a Perkin Elmer Lambda 650 spectrophotometer. The diffuse absorption spectra were recorded in the wavelength range 200–900 nm with the step size for the scan being 1 nm. BaSO_4

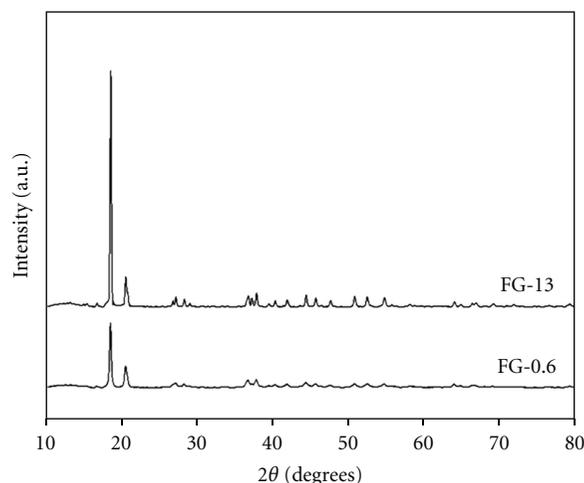


FIGURE 1: The XRD patterns of fine gibbsite ($13 \mu\text{m}$ and $0.6 \mu\text{m}$).

was used as a blank for the measurement. The particles morphology was obtained using a JEOL JSM-35CF SEM operating at 20 kV and JEOL JEM 2010 TEM operating at 200 kV.

3. Results and Discussion

The median particle sizes (d_{50}) of fine gibbsite used as starting materials for producing CoAl_2O_4 in this study were determined by a laser diffraction-based size analyzer to be 0.6 and $13 \mu\text{m}$. Figure 1 shows the XRD patterns of fine gibbsite samples with different particle sizes. The intensities of the XRD peaks decreased, and the peaks became wider as the average particle size of gibbsite decreased from $13 \mu\text{m}$ (FG-13) to $0.6 \mu\text{m}$ (FG-0.6). The XRD patterns of samples obtained from the solid-state reaction of cobalt chloride with FG-13 (Figure 2(a)) and FG-0.6 (Figure 2(b)) at various calcination temperatures are shown in Figure 2. The XRD peaks at 2θ degrees = 31.3° , 36.8° , 44.9° , 59.3° , and 65.3° were observed and could be assigned to either CoAl_2O_4 or Co_3O_4 because their peak positions are almost identical [26]. CoAl_2O_4 and Co_3O_4 have the same spinel cubic (Fd3m) crystallographic structure with slight difference in the lattice constant ($a = 8.111$ for CoAl_2O_4 and $a = 8.0885$ for Co_3O_4). Therefore they have a similar peak pattern, and the positions of peak are nearly same. The transition alumina phase was also found at $2\theta = 68^\circ$ in some samples. However, the relatively low intensity and broad XRD patterns suggest that crystallinity of the samples was not very good and/or the average crystallite size may be very small. The peak detected at $2\theta = 13^\circ$ corresponded to an impurity peak. Figure 3 shows the SEM images of CoAl_2O_4 nanoparticles synthesized via the solid-state reaction between cobalt chloride and FG-13 and FG-0.6 at 650°C . Agglomeration of fine particles forming large irregular particle was observed. However, there is inappreciable change in morphology after calcination at different temperatures.

Figure 4(a) shows the TG/DTA curve of the cobalt chloride which included three endothermic peaks and one exothermic peak. The first and the second endothermic

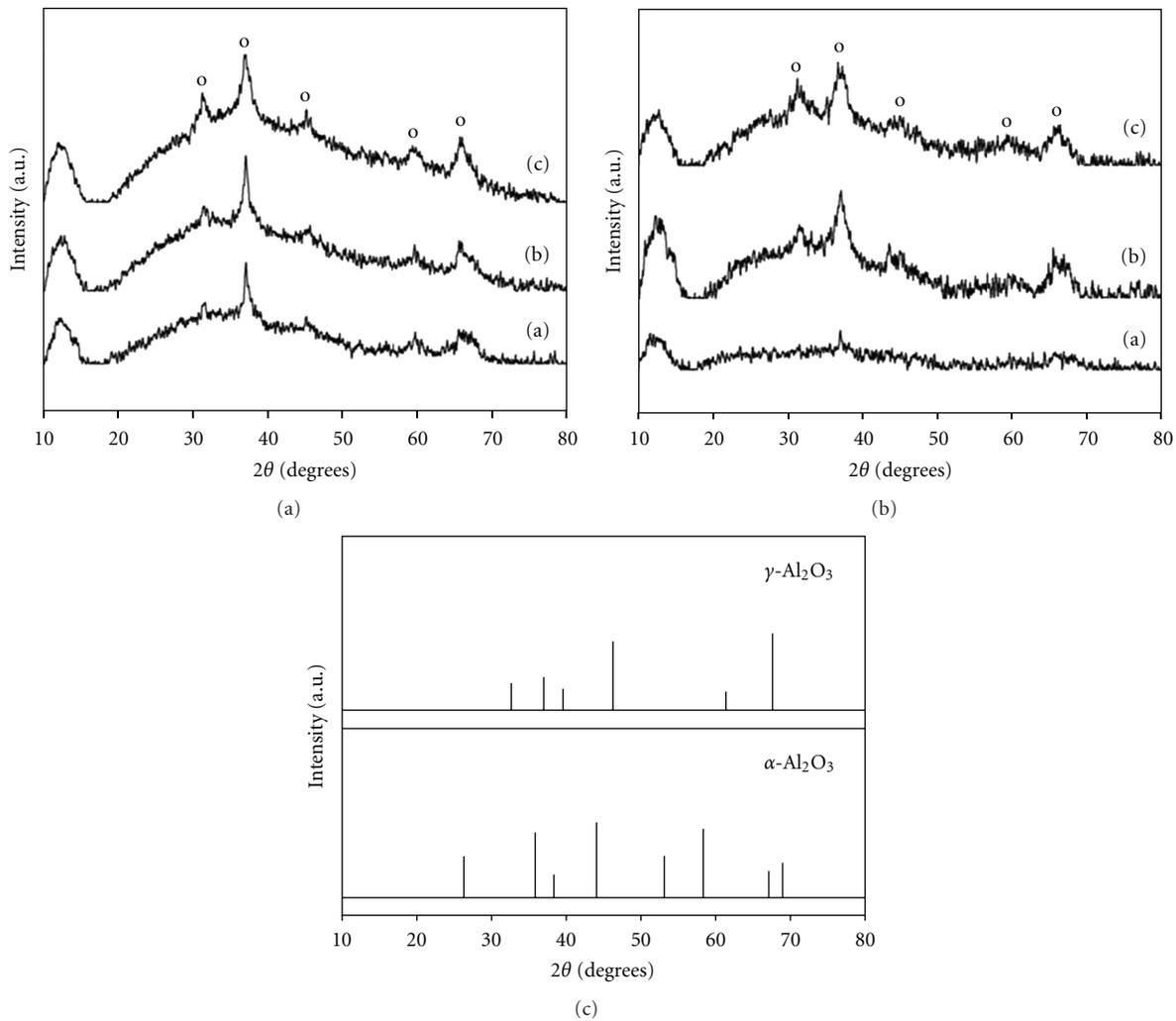


FIGURE 2: The XRD patterns of the CoAl_2O_4 nanoparticles synthesized via the solid-state reaction between cobalt chloride and FG-13 (a) and FG-0.6 (b), after calcination at various temperatures: 450°C (a), 550°C (b), 650°C (c); o = CoAl_2O_4 .

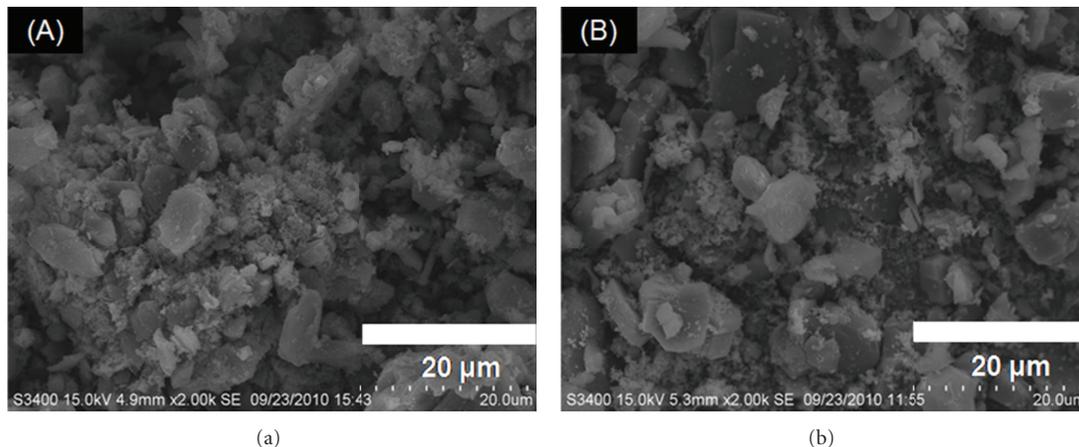


FIGURE 3: SEM images of the CoAl_2O_4 nanoparticles synthesized via the solid-state reaction between cobalt chloride and FG-13 (a), FG-0.6 (b) at 650°C.

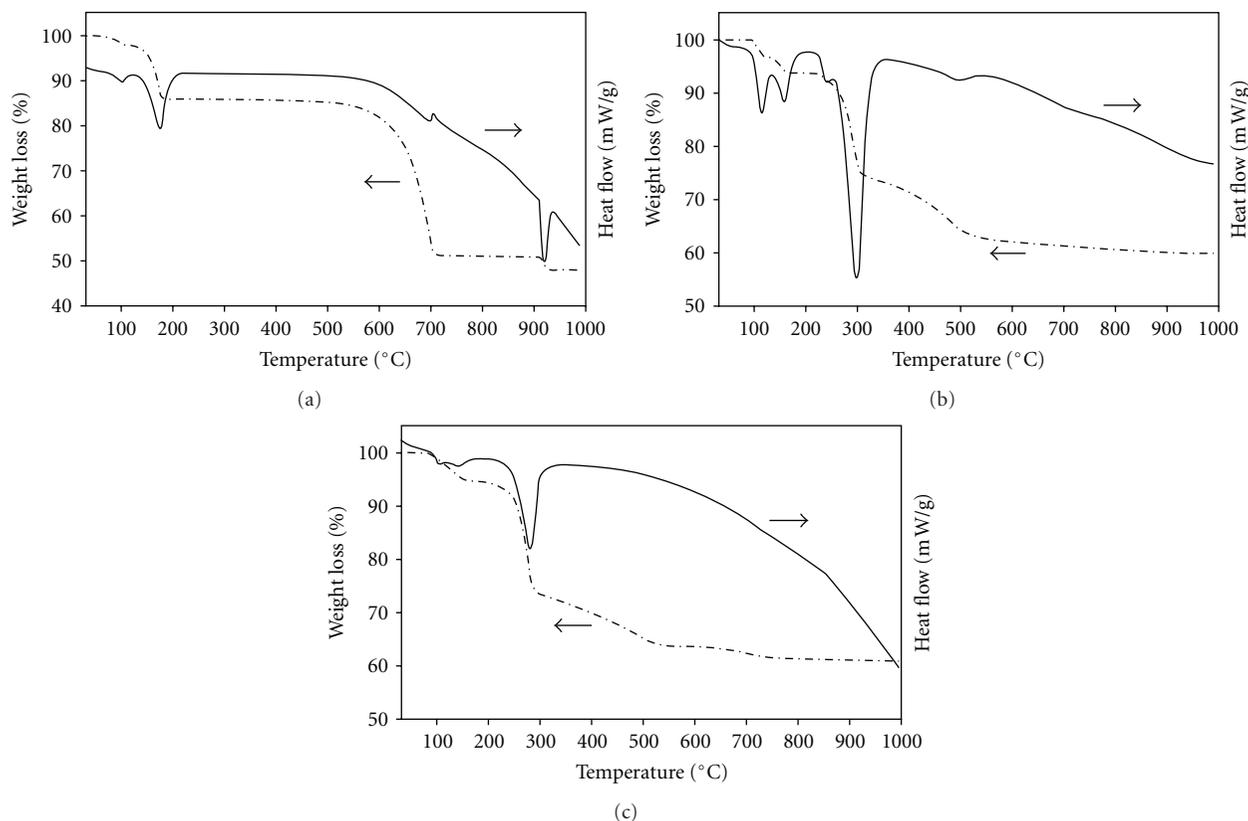


FIGURE 4: The TG/DTA curves of samples: bulk cobalt chloride (a), a mechanical mixture of cobalt chloride and FG-13 (b), and a mixture of cobalt chloride and FG-0.6 (c).

peaks with maxima at 100 and 175°C were accompanied by weight losses of 1.79 and 12.92%, respectively. These peaks corresponded to the loss of water. The exothermic peak at 708°C, which was accompanied by a 48.44% loss in weight, corresponded to the loss of chloride and the subsequent formation of Co_3O_4 . Finally, the last endothermic peak at 920°C, which was accompanied by a 50.49% loss in weight, corresponded to a small oxygen loss and the conversion of Co_3O_4 into CoO [27]. Figures 4(b) and 4(c) illustrate the TG/DTA curves of a mechanical mixture of cobalt chloride and FG-13 and FG-0.6, respectively. The dehydration of a mechanical mixture between cobalt chloride with FG-13 (Figure 4(b)) includes a series of endothermic peaks. The first, second, and third of endothermic peaks were corresponding to the loss of water in the sample. The endothermic peak at around 300°C was the formation of boehmite. In addition, the endothermic peak at around 500°C indicated the formation of cobalt aluminate. It is interesting that the exothermic peak at around 708°C corresponding to chloride elimination disappeared, and the formation of CoAl_2O_4 occurred at much lower temperature. It is suggested that in the presence of gibbsite, cobalt chloride was decomposed easier probably due to the hydrolysis reaction by water dehydrated from gibbsite. Moreover, as gibbsite particle size decreased from 13 μm to 0.6 μm , the series of endothermic peaks decreased and the endothermic peaks at around 230 and 500°C disappeared (compared to Figures 4(b) and 4(c)).

Such results suggest that the dehydration of a mechanical mixture between gibbsite and cobalt chloride was accelerated when the particle size of gibbsite was decreased. As a consequence, cobalt aluminate was formed at lower calcination temperature. The images of synthesized CoAl_2O_4 nanoparticles are shown in Figure 5. Bright blue color was clearly observed for the FG-13 and FG-0.6 calcined at 650°C and FG-0.6 calcined at 550°C, indicating the formation of CoAl_2O_4 structure.

The XPS analyses were carried out to examine surface species on the samples. The samples were analyzed in the Co 2p, Al 2s, and O 1s binding energy regions. The binding energy, the atomic concentration, and the FWHM of Co 2p_{3/2} and Al 2s are given in Table 1. According to the literature [20, 28] cobalt in an oxide state (Co 2p_{3/2} in Co_3O_4) exhibited lower binding energy (780.0 eV) than that in CoAl_2O_4 (781.9 eV). The XPS results confirm that the samples prepared by solid-state reaction between cobalt chloride and FG-13 calcined at 650°C and FG-0.6 calcined at 550°C were CoAl_2O_4 which were in good agreement with the blue color observed in Figure 5. Moreover, the relative amount of Co^{2+} ions in tetrahedral sites was found to increase with increasing calcination temperature. Decreasing the particles size of fine gibbsite probably increased the rate of diffusion step during a solid-state reaction [24]; thus the CoAl_2O_4 was formed at lower calcination temperature for FG-0.6 than FG-13. The average crystallite sizes of synthesized CoAl_2O_4 were

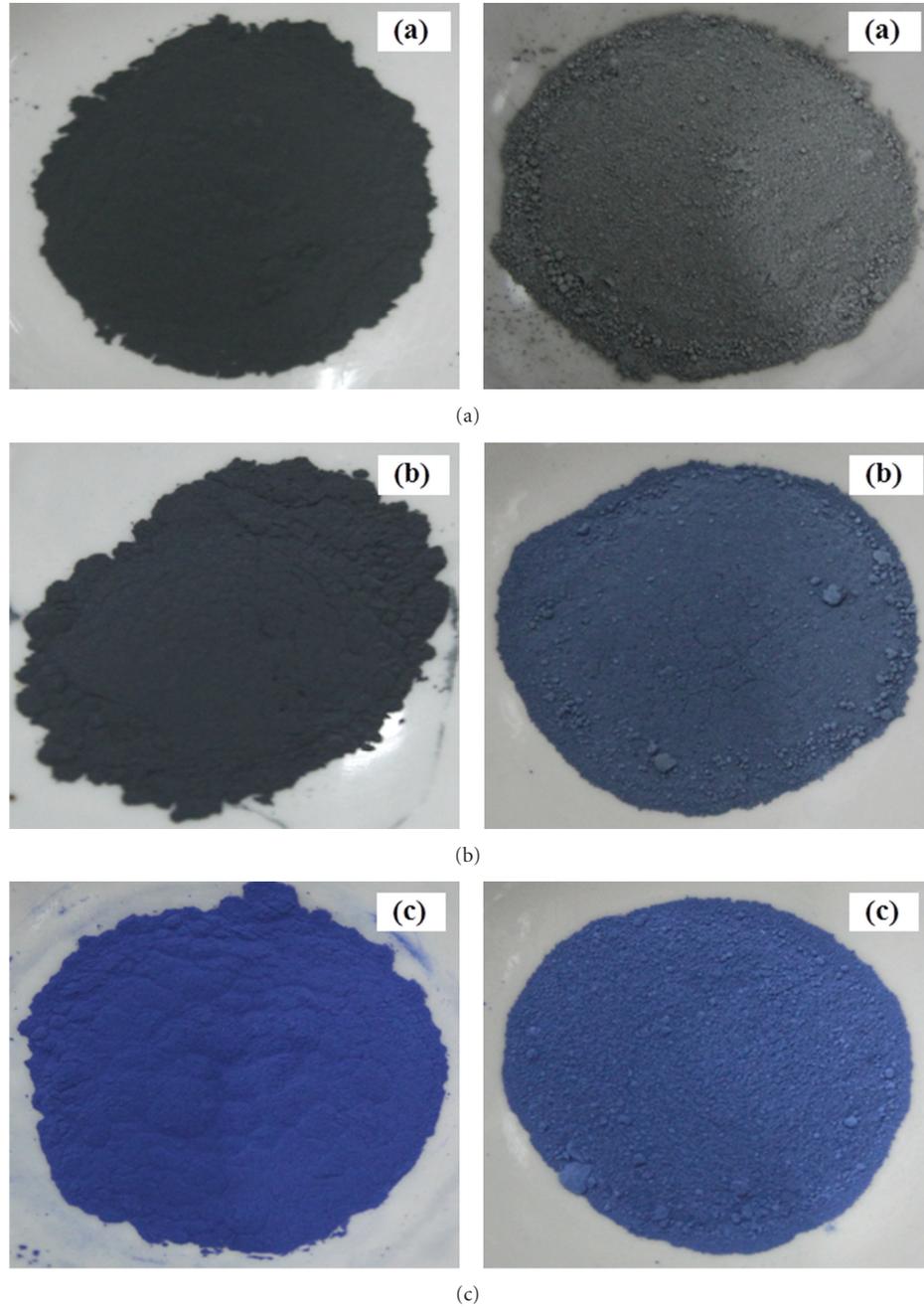


FIGURE 5: The images of the CoAl_2O_4 nanoparticles synthesized via the solid-state reaction between cobalt chloride and FG-13 (left-hand side) and FG-0.6 (right-hand side) after calcination at various temperatures: 450°C (a), 550°C (b), and 650°C (c).

TABLE 1: The crystallite size and XPS results of the CoAl_2O_4 particles obtained via solid-state reaction of fine gibbsite and cobalt chloride.

Samples	d_{XRD} (nm)	Co(II) 2p _{3/2}		Al 2s		Atomic Conc%	
		B.E. (eV)	FWHM	B.E. (eV)	FWHM	Al/O	Co/Al
FG-13-650°C	6	781.9	2.819	119.1	2.828	0.50	0.032
FG-0.6-550°C	6	781.5	3.223	118.6	2.772	0.50	0.050
FG-0.6-650°C	6	782.1	3.385	119.2	2.678	0.48	0.053
^a Co ₃ O ₄		780.0 ± 0.7					
^a CoAl ₂ O ₄		781.9 ± 0.5					

^aReferences [20, 27].

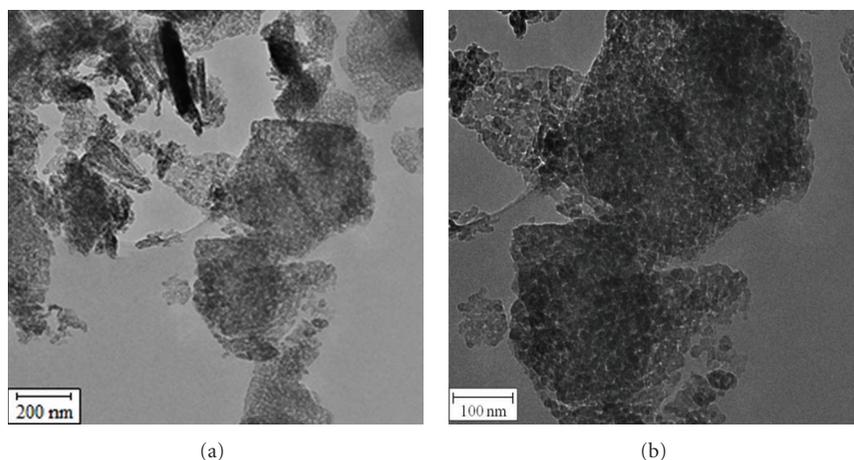


FIGURE 6: TEM images of the synthesized CoAl_2O_4 nanoparticles (FG-0.6 calcined at 650°C).

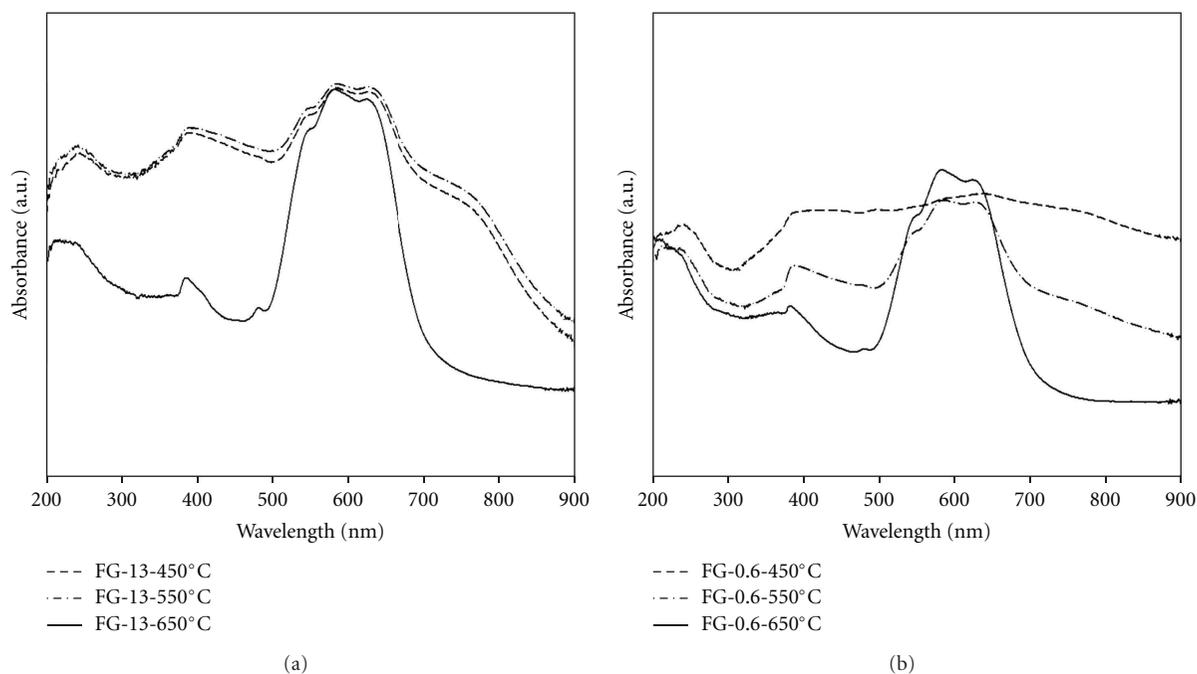


FIGURE 7: Absorption spectra in the wavelength range 200–900 nm of the CoAl_2O_4 nanoparticles synthesized via the solid-state reaction between cobalt chloride and FG-13 (a) calcined at various temperatures and (b) the solid-state reaction of cobalt chloride and FG-0.6 calcined at various temperatures.

calculated from the full width at half maximum of the XRD peak at $2\theta = 36.8^\circ$ using the Scherrer's equation and are reported in Table 1 (d_{XRD}). The TEM images of synthesized CoAl_2O_4 are shown in Figure 6. The TEM results clearly show that the synthesized CoAl_2O_4 consisted of very fine particles with average size below 10 nm which are in good agreement with the average crystallite size calculated from the Scherrer's equation.

UV-Vis spectroscopy was carried out in order to study the correlation between cation distribution and the optical properties of synthesized CoAl_2O_4 nanoparticles. Figure 7 shows the absorption spectra of the CoAl_2O_4 particles obtained

from the solid-state reaction of cobalt chloride and FG-13 and FG-0.6 at various calcination temperatures. The UV-Vis results were consistent with the XPS analyses. The Co^{2+} in a tetrahedral ligand field is responsible for its blue color. It has been reported that the coloration of CoAl_2O_4 was strongly dependent on the temperature of the heat treatment and on the stoichiometry of Co and Al in the $\text{Co}_{3-5}\text{Al}_5\text{O}_4$ sample with the brightest blue coloration being obtained for $S = 2.25$ [16]. The intense absorption peak at around 600 nm for both of the prepared CoAl_2O_4 particles is the characteristic of Co^{2+} ions in the tetrahedral sites in crystalline materials [9]. From the UV-Vis spectra of the prepared CoAl_2O_4 particles

in Figure 7, a triple band was observed at around 540–630 nm, attributed to the spin-allowed [$^4A_2(F) \rightarrow ^4T_1(P)$] transition. This triple band can be attributed to a Jahn Teller distortion of the tetrahedral structure [29]. It was found that the intensity of this triple band decreased with decreasing particles size of the starting fine gibbsite for a given calcination temperature (i.e., at 650°C). According to the XPS results, the atomic concentration of Co/Al increased with decreasing particles size of the starting fine gibbsite. It has been also reported that the intensity of this triple band decreased as the S value was increased and might be probably due to the formation of white Al_2O_3 from excess Al in the samples, lowering the intensity of color although the S values were larger than 2.25 and remained blue [16]. The results in this study also suggest that reduction of particle size of the starting material could have an influence on the band shift. However, further detailed study is necessary to confirm whether the blue shift is because of the reduction of particle size [27–30].

4. Conclusions

Nanocrystalline $CoAl_2O_4$ particles were successfully synthesized at low temperature by solid-state reaction using calcination of the mechanical mixture between fine gibbsite and cobalt chloride. The particle sizes of the starting fine gibbsite were 0.6 and 13 μm and the calcination temperature was varied in the range of 450–650°C. The XRD and XPS results revealed that the crystallization of $CoAl_2O_4$ from the mixture between cobalt chloride and FG-13 and FG-0.6 occurred at 650°C and 550°C, respectively. The reduction of the starting particle size of fine gibbsite resulted in the lower crystallization temperature of $CoAl_2O_4$ formation due to the increase of contact area between reacting particles. However, increasing of calcination temperature promoted the insertion amounts of Co^{2+} in alumina matrix in $CoAl_2O_4$ structure, which resulted in the brighter blue particles and increasing of UV spectra band.

Conflict of Interests

J. Panpranot, the corresponding author of the paper, confirms that he does not have a direct financial relation with the commercial identity mentioned in the paper submitted that might lead to a conflict of interests for any of the authors.

Acknowledgments

The financial supports from the Thailand Research Fund (TRF), the Office of Higher Commission Education, and the CU-NRU project (AM1088A) are gratefully acknowledged.

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