



Dedicated to the memory of
Professor Eugen Segal (1933-2013)

Co-Al LAYERED DOUBLE HYDROXIDES AS PRECURSORS OF CERAMIC PIGMENT CoAl_2O_4 . PART I: PHASE COMPOSITION

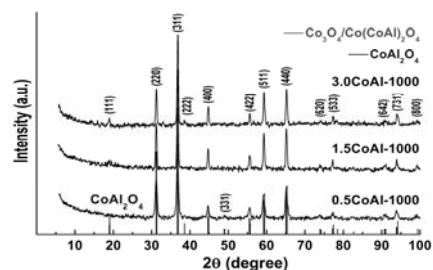
Margarita GABROVSKA,^{a,*} Dorel CRIȘAN,^b Nicolae STĂNICĂ,^b Dimitrinka NIKOLOVA,^a
Lyubima BILYARSKA,^a Maria CRIȘAN^b and Rumeana EDREVA-KARDJIEVA^a

^aInstitute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 11, 1113 Sofia, Bulgaria

^b“Ilie Murgulescu” Institute of Physical Chemistry, Roumanian Academy, 202 Splaiul Independentei,
060021 Bucharest-12, Roumania

Received April 10, 2014

Co-Al layered double hydroxides with composition of $\text{Co}^{2+}/\text{Al}^{3+} = 0.5, 1.5$ and 3.0 have been prepared by co-precipitation followed by stepwise heating in the range of $200\text{--}1200^\circ\text{C}$. The effect of the Co content on the structure evolution of Co-Al materials used as precursors for obtaining of ceramic pigment CoAl_2O_4 was studied varying the $\text{Co}^{2+}/\text{Al}^{3+}$ molar ratio and the temperature of thermal treatment. It was specified that upon heating at 250°C the layered structure is destroyed completely and a badly organized non-stoichiometric spinel-like phases is formed. It was established that single phase CoAl_2O_4 spinel is registered only in the solid with the lowest Co loading after calcination at 1000°C , while the presence of solid solution $\text{Co}_3\text{O}_4\text{--CoAl}_2\text{O}_4$ with spinel structure is observed in the rest of the samples treated at 1200°C . The degree of phase crystallization correlates with the nano-sized particle increase, being accompanied by a decrease of specific surface area at the temperature raising.



INTRODUCTION

Cobalt aluminate (CoAl_2O_4) belongs to the class of chemically and thermally stable solids with a crystal structure that falls into the category of normal spinels ($\text{A}^{2+}\text{B}^{3+}_2\text{O}_4$ type). The crystal lattice consists of a cubic close packing of oxygen atoms surrounded by tetrahedrally (Td) coordinated Co^{2+} cations (A) and octahedrally (Oh) coordinated Al^{3+} cations (B).¹ The mode of sites occupation depends on the temperature of thermal treatment.²

CoAl_2O_4 spinel is widely used for obtaining of the blue pigment, known as Thenard's blue, cobalt blue or royal blue, applied in the ceramic, glass,

plastics, rubber and paint industry as a coloring agent.^{3,4} Cobalt aluminate can be synthesized by various routes such as polymerized complex technique, molten salt, polyol, low-temperature combustion, sol-gel, citrate-gel, metal-organic chemical vapor deposition, EDTA and glycine chelated precursor, hydrothermal, polymer aerosol pyrolysis, and reverse micelle processes.⁵ Nonetheless, the selection of preparation method is usually based upon the desired properties of the final materials.³

The standard method to prepare CoAl_2O_4 spinel is the solid-state reaction of mechanically mixed Co and Al oxide powders or carbonates, followed

* Corresponding author: margo@ic.bas.bg

by milling and grinding. However, this method often leads to coarse crystals and the presence of impurities with a detrimental effect on the material properties. The synthetic route requires also prolonged processing time ranging from several hours to days and calcination at high temperature (>1200°C), leading to sintered materials with low surface area and unwelcome crystallite growth.⁶

In this paper is report a co-precipitation route consisting in the synthesis of layered double hydroxides followed by their controlled thermal decomposition as an alternative method.

The layered double hydroxides (LDHs), also known as hydrotalcite-like materials (HTL) or as anionic clays, are a large group of natural and synthetic materials. They consist of positively charged brucite-like hydroxide layers $[M_{1-x}M_x^{3+}(\text{OH})_2]^{x+}$, containing uniformly distributed M^{2+} (Mg^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , etc) and M^{3+} (Al^{3+} , Cr^{3+} , In^{3+} , etc) cations, octahedrally coordinated by hydroxide groups. The system electroneutrality is achieved by intercalation of the charge compensating exchangeable anions A^{n-} (CO_3^{2-} , NO_3^- , SO_4^{2-} , Cl^- , etc) located in the hydrated interlayer regions $[A^{n-}]_{x/n} \cdot m\text{H}_2\text{O}$. Herewith, x represents the fraction of the M^{3+} cation, and m is the number of H_2O molecules. The M^{2+} and M^{3+} cations as well as the interlayer anions (A^{n-}) together with the value of the stoichiometric coefficient (x) may be varied over a wide range, giving rise to a large class of isostructural materials. This flexibility in composition allows LDHs with a wide diversity of properties to be prepared which is one of their most attractive features. The controlled thermal decomposition of LDHs includes dehydration, dehydroxylation and loss of the charge compensating anions. These processes result in formation of highly dispersed nano-sized mixed metal oxides and spinel phases with an homogeneous distribution of both M^{2+} and M^{3+} cations, small crystal size and stability against sintering and homogeneous solid solutions. The composition of the final high temperature products depends considerably on the nature of the present cations.⁷ If one of cations represents oxidizable transition metal, the solid exhibits a definite color, depending on the molar fraction of the metal cations, the oxidation state and the symmetry of occupied sites. The advantages of the use of LDHs as precursors for ceramic pigment enables to modulate the properties of the calcined solids through a precise selection of M^{2+}/M^{3+} ratio of the corresponding layered compounds.

The aim of this work is to establish the effect of the $\text{Co}^{2+}/\text{Al}^{3+}$ molar ratio varying and the thermal treatment in a wide temperature range of 200–1200°C on the structure evolution of Co-Al LDHs as precursors for obtaining of CoAl_2O_4 ceramic pigment.

EXPERIMENTAL

Sample preparation

Carbonate forms of LDH compounds with $\text{Co}^{2+}/\text{Al}^{3+}$ molar ratios of 0.5, 1.5 and 3.0 were synthesized by co-precipitation of a mixed Co-Al nitrate solution with Na_2CO_3 solution at constant values of both temperature of 80°C and pH = 8.0 under vigorous stirring. More detailed description of the preparation procedure was presented in our recent paper.⁸ The obtained precipitate was further dried at 80°C for 20 h and named hydrotalcite sample, designated as $x\text{CoAl-HT}$, where x represents the $\text{Co}^{2+}/\text{Al}^{3+}$ molar ratio, for example 3.0CoAl-HT (Table 1). The dried layered systems were step-wise thermally treated in air for 2 h in the temperature range 200–1200°C with a heating rate of 3°C/min. The materials were labeled as $x\text{CoAl-y}$, where y represents temperature of the thermal treatment, for example 3.0CoAl-200.

Sample characterization

The chemical composition of the as-synthesized materials was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using JY (Jobin Yvon) 38 spectrometer. The specific surface area was measured employing the single point BET method (Micromeritics Instrument, FlowSorb 2300), using N_2/He mixture (30/70) at the boiling temperature of liquid nitrogen. The phase composition of the as-synthesized and calcined samples was established by Powder X-ray diffraction (PXRD) analysis. The data was collected on a Bruker D8 Advance diffractometer employing CuK_α radiation ($\lambda = 0.15418$ nm), operated at $U = 40$ kV and $I = 40$ mA. The mean crystallite sizes (L) were determined using computer program X'Pert HighScore (PW3209) Version 1.0f (2004). The crystalline phases were identified using Joint Committee on Powder Diffraction Standards (JCPDS) files.

RESULTS AND DISCUSSION

The chemical analysis data of the as-synthesized samples listed in Table 1 reveal that $\text{Co}^{2+}/\text{Al}^{3+}$ ratios measured experimentally by ICP are nearly equal to the corresponding ratios in the synthesis solutions. The color of the materials dried at 80°C varied depending on the $\text{Co}^{2+}/\text{Al}^{3+}$ molar ratio. The change of the sample tint presumes thermodynamically favored partial oxidation of Co^{2+} ions to Co^{3+} ones during the synthesis of 3.0CA-HT.

Table 1

Chemical composition of the as-prepared Co-Al samples

Sample	Chemical composition as $\text{Co}^{2+}/\text{Al}^{3+}$ (molar ratio)		Color
	Theoretical	Experimental	
0.5CoAl-HT	0.50	0.48	Intense pink
1.5CoAl-HT	1.50	1.46	Pale pink
3.0CoAl-HT	3.00	2.87	Beige

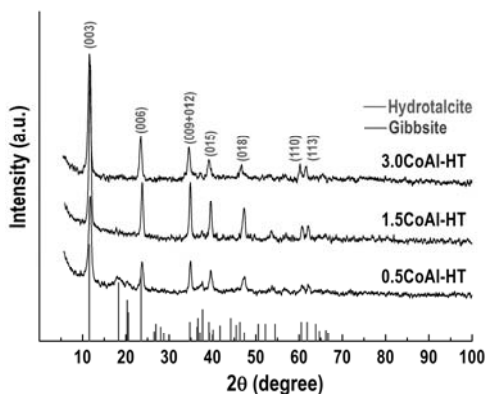


Fig. 1 – PXRD patterns of the HTL samples.

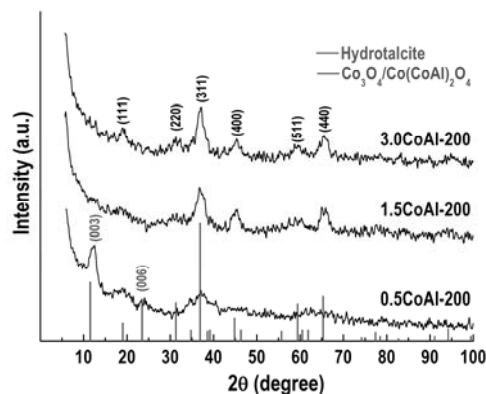


Fig. 2 – PXRD patterns of the samples calcined at 200°C.

Table 2

Structural characteristics and specific surface area of the as-synthesized samples

Sample	a (nm)	c (nm)	V (nm ³)	SSA (m ² /g)	$L_{(003)}$ (nm)
0.5CoAl-HT	0.3046±0.0027	2.2559±0.0016	0.1811±0.0604	89	13
1.5CoAl-HT	0.3049±0.0028	2.2565±0.0012	0.1813±0.0043	29	22
3.0CoAl-HT	0.3076±0.0019	2.2962±0.0065	0.1872±0.0032	60	16
¹ Hydrotalcite	0.3046	2.2772	0.1829	JCPDS file 01-089-0460	
² Hydrotalcite	0.3070	2.3230	0.1896	JCPDS file 00-014-0191	

In our previous paper⁸ it was documented that a single HTL phase containing carbonate anions in the interlayer space is registered for 3.0CoAl-HT and 1.5CoAl-HT precipitates, better organized in 1.5CoAl-HT (Fig. 1). Additional diffraction lines appear in 0.5CA-HT that may be attributed to the presence of gibbsite phase, $\text{Al}(\text{OH})_3$ (JCPDS file 00-033-0018) as result of the excess of Al in the initial Co-Al solution.

The calculated lattice parameters for 0.5CoAl-HT and 1.5CoAl-HT samples (Table 2) show values similar to these reported for HT with ratio of $\text{M}^{2+}/\text{M}^{3+} = 2.0$ (JCPDS file 01-089-0460) as well as for 3.0CoAl-HT sample are rather close to these with ratio of $\text{M}^{2+}/\text{M}^{3+} = 3.0$ (JCPDS file 00-014-0191). The increase of $\text{Co}^{2+}/\text{Al}^{3+}$ ratio induces the increase of all lattice parameters (a , c and V), as it is well-known for the LDH-type materials. The increase of the parameters a and V is ascribed to the higher Oh ionic radius of Co^{2+} ion ($r = 0.074$ nm) with respect to Al^{3+} ($r = 0.050$ nm).⁹ The substitution of Al^{3+} by Co^{2+} ions decreases the positive charge density of the brucite-like layer

thus diminishing the electrostatic interaction between the hydroxide layer and the interlayer resulting in an increase of the parameter c .

The sharp increase in the lattice parameters (a , c and V) for 3.0CA-HT sample may be interpreted based on the double effect of the partial oxidation of Co^{2+} to Co^{3+} ions in the Oh positions of the brucite-like layer during the synthesis, namely (i) the greater ionic radius of Co^{3+} ions ($r = 0.063$ nm)⁹ causes the increase in parameter a , and (ii) the higher oxidation state of Co^{3+} ions enhances the brucite-like layer positive charge density and requires more CO_3^{2-} anions for charge compensation and more H_2O molecules to prevent inter-anionic repulsion in the interlayer space leading to increase in parameters c and V . The presence of Co^{3+} ions might be also supported by the beige color of the 3.0CA-HT sample. An inspection of the diffraction lines of the as-synthesized compounds (Fig. 1) evidences different degree of crystallinity with the variation of the $\text{Co}^{2+}/\text{Al}^{3+}$ ratio. The estimation of mean crystallite sizes (L) from the full-width at half-

maximum values of (003) diffraction line permit the finding that the increase of the Co loading leads to the crystallite size growth passing through maximum for 1.5CoAl-HT sample. These results are in concordance with the specific surface area (SSA) data, passing through minimum for 1.5CoAl-HT in accordance with its highest crystallinity (Table 2).

It may be observed that the characteristic diffraction lines of HTI structure disappear completely after treatment of 1.5CoAl and 3.0CoAl samples at 200°C (Fig. 2). This observation is attributed to both dehydroxylation of the brucite-type layers and decarbonation of the interlayer space as result of the destruction of the layered structure. New reflections are registered that can be ascribed to the presence of a spinel-like Co_3O_4 phase (JCPDS 00-043-1003) and/or spinel-like mixed oxides denoted as $\text{Co}(\text{Co},\text{Al})_2\text{O}_4$, due to the partial oxidation of Co^{2+} to Co^{3+} ions. An isomorphous substitution of the greater Co^{3+} ions, located in Oh sites in the main Co_3O_4 phase by the smaller Al^{3+} ions causes formation of a very homogeneous and stable spinel-like mixed oxide

$\text{Co}^{2+}(\text{Co}^{3+}, \text{Al}^{3+})_2\text{O}_4$, as it has been described in detail. Both spinel-like phases demonstrate similar reflections and intensities, thus it is not possible to distinguish between them.^{10,11}

It may be noted that the thermal treatment of 0.5CoAl at 200°C induces creation of an intermediate meta-stable mixture of dehydrated hydrotalcite-like phase [(003) and (006) reflections of the layered structure are visible] and spinel-like $\text{Co}(\text{Co},\text{Al})_2\text{O}_4$. The diffraction lines of the all thermally treated at 250°C samples suggests collapse of the layered structure for 0.5CoAl-250 as well as enhancement of the samples crystallinity, being better organized in 3.0CoAl-250 (Fig. 3). Further increase of the decomposition temperature up to 800°C provokes the appearance only of new lines of $\text{Co}(\text{Co},\text{Al})_2\text{O}_4$ phase for 1.5CoAl-800 and 3.0CoAl-800, more pronounced in 3.0CoAl sample, indicating that Al^{3+} cations are no more statistically distributed as they are located mainly in Oh positions of the mixed oxide spinel-like structures. A spinel CoAl_2O_4 phase (JCPDS file 00-044-0160) is detected for 0.5CoAl-800 (Fig. 4).

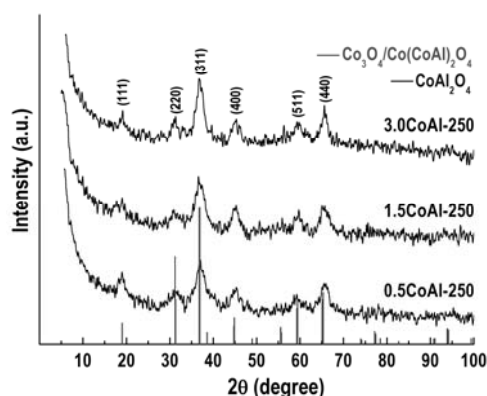


Fig. 3 – XRD patterns of the samples calcined at 250°C.

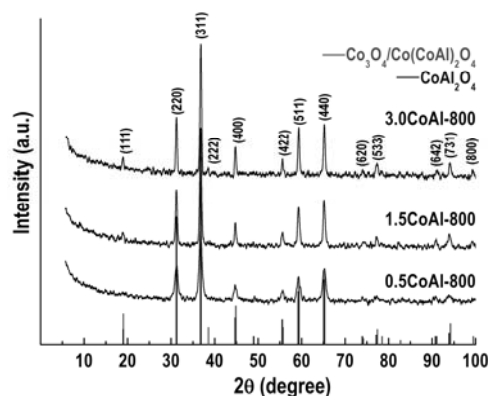


Fig. 4 – XRD patterns of the samples calcined at 800°C.

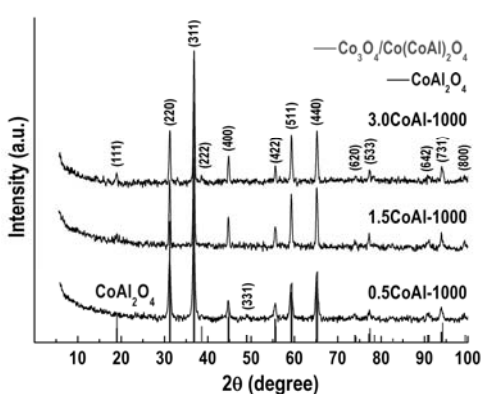


Fig. 5 – XRD patterns of the samples calcined at 1000°C.

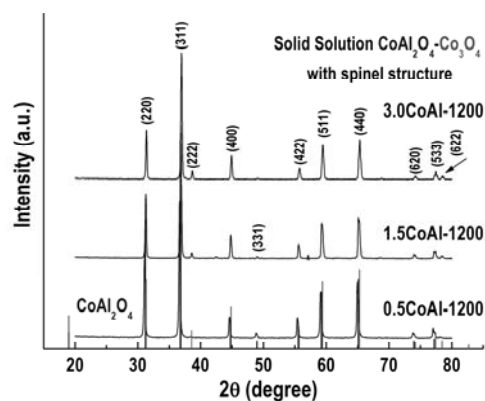


Fig. 6 – XRD patterns of the samples calcined at 1200°C.

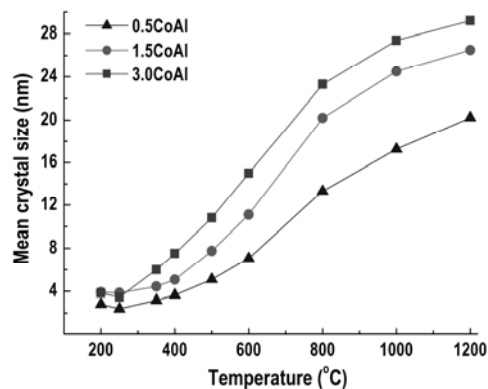


Fig. 7 – Mean crystallite size of the calcined samples.

The diffraction peaks of all calcined samples became narrower and more intensive, due to the growth of crystallites and improvement of the mixed oxide phases crystallization. PXRD patterns of 0.5CoAl after calcination at 1000°C (Fig. 5) and 1200°C (Fig. 6) respectively, detect reflections of a well crystallized spinel CoAl_2O_4 . An existence of solid solution $\text{CoAl}_2\text{O}_4\text{-Co}_3\text{O}_4$ with a spinel structure is registered for 1.5CoAl and 3.0CoAl after thermal treatment at 1200°C. Actually, this is non-stoichiometric spinel, mixture where CoAl_2O_4 crystallites exist together with Co_3O_4 oxide. No separate Al-containing phase was recorded for all solids.

The mean crystallite size of spinel-type phases were determined from the full-width at half-maximum values of (311) diffraction line. It is observed that the increase of calcination temperature and the Co content leads to the crystal size enlargement (Fig. 7). The mixed oxide crystallites remain in the nano-metrical scale in the whole temperature range. The smallest crystallites are observed in the interval of 200–400°C.

The degree of phase crystallization correlates also with the values of SSA measurements (Fig. 8). The highest SSA values are observed at intermediate calcination temperatures, at which PXRD indicated the formation of non-well organized structures. The further increase of the temperature causes the decrease of SSA values, due to the crystallization of well-defined phases.¹²

CONCLUSIONS

The variance of the $\text{Co}^{2+}/\text{Al}^{3+}$ molar ratio of Co-Al layered double hydroxides leads to different

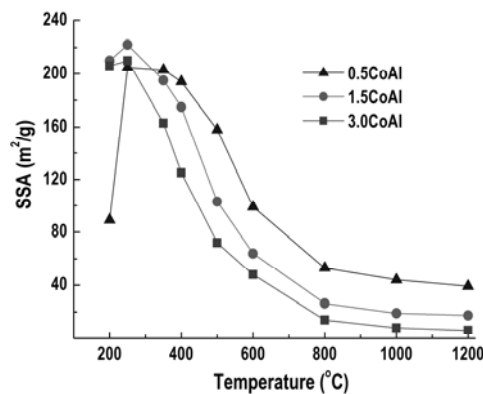


Fig. 8 – Specific surface area of the calcined samples.

behavior at thermal treatment, phase composition and crystal size development.

The layered structure of Co-Al compounds is completely destroyed upon calcination in the interval of 200–250°C resulting in appearance of badly organized spinel-like mixed oxide $\text{Co}(\text{Co},\text{Al})_2\text{O}_4$, due to the presence of Co^{3+} ions because of Co^{2+} oxidation. The controlled thermal treatment of the Co-Al layered systems results in the formation of spinel-type phases, whose crystallinity increases with the calcination at higher temperatures. A well defined single CoAl_2O_4 spinel is registered only in the solid with the lowest Co loading. The presence of solid solution $\text{CoAl}_2\text{O}_4\text{-Co}_3\text{O}_4$ with spinel structure is observed in both samples with higher Co amount. The mixed oxide crystallites remain in the nano-metrical scale in the whole temperature range irrespective of their parent composition.

Note: This study was realized in the frame of inter-academic collaboration between Institute of Catalysis, Bulgarian Academy of Sciences, and “Ilie Murgulescu” Institute of Physical Chemistry, Roumanian Academy: “*Nano-sized oxide materials with catalytic and applied character*”.

REFERENCES

1. J-H. Kim, B-R. Son, D-H. Yoon, K-T. Hwang, H-G. Noh, W-S. Cho and U-S. Kim, *Ceram. Int.*, **2012**, *38*, 5707-5712.
2. K. Becker, *Solid State Ionics*, **2001**, *141*, 21-30.
3. W. Cho and M. Kakihana, *J. Alloys Compd.*, **1999**, *287*, 87-90.
4. W. Lv, Q. Qiu, F. Wang, S. Wei, B. Liu and Z. Luo, *Ultrason. Sonochem.*, **2010**, *17*, 793-801.
5. N. Srisawad, W. Chaitree, O. Mekasuwandumrong, P. Praserttham and J. Panpranot, *Journal of Nanomaterials*, **2012**, Article ID 108369, 8 pages.

6. C. Wang, S. Liu, L. Liu and X. Bai, *Mater. Chem. Phys.*, **2006**, *96*, 361-370.
7. F. Cavani, F. Trifirò and A. Vaccari, *Catal. Today*, **1991**, *11*, 173-301.
8. M. Gabrovska, R. Edreva-Kardjieva, K. Tenchev, P. Tzvetkov, A. Spojakina and L. Petrov, *Appl. Catal. A-Gen.*, **2011**, *399*, 242-251.
9. R. Shannon, *Acta Crystallogr. A*, **1976**, *32*, 751-767.
10. S. Kannan and C. Swamy, *Catal. Today*, **1999**, *53*, 725-737.
11. J. Pérez-Ramírez, G. Mul, F. Kapteijn and J. Moulijn, *J. Mater. Chem.*, **2001**, *11*, 821-830.
12. F. Labajos, M. Sastre, R. Trujillano and V. Rives, *J. Mater. Chem.*, **1999**, *9*, 1033-1039.