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Effect of added zinc on the properties of cobalt-containing ceramic pigments prepared from layered double hydroxides

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ABSTRACT

Layered double hydroxides (LDHs) with the hydrotalcite-type structure containing Co and Al, or Zn, Co and Al in the brucite-like layers and carbonate in the interlayer have been prepared by coprecipitation. The Zn/Co molar ratio was kept to 1 in all samples, while the divalent/trivalent molar ratio was varied from 2/1 to 1/2. The samples have been characterised by element chemical analysis, powder X-ray diffraction, differential thermal and thermogravimetric analysis, temperature-programmed reduction and FT-IR spectroscopy. A single hydrotalcite-like phase is formed for samples with molar ratio 2/1, which crystallinity decreases as the Al content is increased, developing small amounts of diaspore and dawsonite and probably an additional amorphous phase. Calcination at 1200 °C in air led to formation of spinels; a small amount of $NaAlO_2$ was observed in the Al-rich samples, which was removed by washing. The nature of the spinels formed (containing Co^{II}, Co^{III}, Al^{III} and Zn^{II}) strongly depends on the cations molar ratio in the starting materials and the calcination treatment, leading to a partial oxidation of Co^{II} species to Co^{III} ones. Colour properties ($L^*a^*b^*$) of the original and calcined solids have been measured. While the original samples show a pink colour (lighter for the series containing Zn), the calcined Co,Al samples show a dark blue colour and the Zn,Co,Al ones a green colour. Changes due to the different molar ratios within a given calcined series are less evident than between samples with the same composition in different series. These calcined materials could be usable as ceramic pigments.

1. Introduction

Ceramic pigments are inorganic crystalline structures able to develop a stable colour at high temperatures. They should be thermally stable, resistant to alkaline and acid attacks, insoluble in glazes, to show a given narrow particle size distribution and should not evolve gases. Three different types are commonly described, namely, (i) those formed by an inorganic matrix including a chromophore in the structure or as a dopant in a solid solution, (ii) those formed by deposition of a colloidal layer of the chromophore on a support, and (iii) those where the chromophore is encapsulated in a crystalline carrier. The colour usually arises from charge transfer processes, electron transfer between energy bands, or *d*–*d* or *f*–*f* transitions. Llusar et al. [1] have reported a detailed analysis of cobalt-containing blue ceramic pigments with different crystalline phases, namely, olivine, willemite, and spinel; actually, the spinel structure is one of the most frequently found in ceramic pigments. The spinel structure is adopted by many compounds, but is extremely important for oxides with the stoichiometry $A^{II}B_2^{III}O_4$. The structure consists of a cubic close packing of oxide anions where the octahedral and tetrahedral holes are occupied by divalent or trivalent cations, giving rise to the so-called normal spinels (A^{II} in tetrahedral holes and B^{III} in octahedral ones) or inverse spinels (A^{II} and one half of B^{III} in octahedral holes and the remaining B^{III} cations in tetrahedral ones), together with partially inverse structures. The nature of the cations can be varied and, in addition, non-stoichiometric spinels (actually, mixtures where the spinels crystallites exist together with another oxide) are also known. If one or both cations correspond to transition metals, the solid shows a given colour, depending on the molar fraction of the metal cations, their formal oxidation state and the nature of holes occupied. Development of procedures to prepare spinels (both stoichiometric and non-stoichiometric) could be a good approach for obtaining ceramic pigments fulfilling the above listed requirements.

Although spinels can be prepared by a conventional ceramic reaction, alternative procedures have been described to obtain more homogeneous solids, with smaller particle size, under milder conditions. Regarding Co-containing spinels, hydrothermal methods [2,3] and sol–gel ones [4–7] have been applied. Meyer et al. [4] have used a microemulsion-assisted sol–gel process, using a single source heterometal alkoxide (containing both Al and the divalent cations) as a precursor; however, Lavrencic

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Stangar et al. [6] have claimed that the use of two different cations precursors is much better, as it permits to vary the molar ratios between the cations, thus leading to formation of selected stoichiometric or non-stoichiometric spinels. The sol–gel and citrate procedures [5] permit formation of an intermediate homogeneous solid, favouring diffusion processes during thermal treatments, thus decreasing the temperature needed to form the desired compounds; similar advantages have been claimed [8] when using oxalate precursors. Pacurariu et al. [9] have used organometallic precursors (actually, Co^{II}, Zn^{II}, and Al^{III} nitrates reacted with 1,2-ethanediol) to prepare spinels with different Co/Zn molar ratios. Other methods, namely, auto-ignited gel combustion using citric acid as fuel and metal nitrate as oxidants [10], microemulsions [11], and the polymeric precursor [12] process, have been also applied. We report here on an alternative method, consisting of calcination of layered double hydroxides (LDHs). These are layered materials which structure corresponds to that of brucite, $Mg(OH)_2$, with partial Mg^{II}/M^{III} substitution. The positive charge of the layers is balanced by intercalated hydrated anions. The most representative member of this family of compounds is hydrotalcite, $Mg_6Al_2(CO_3)(OH)_{16}\cdot 4H_2O$. The cations can be easily changed (most of first transition metal cations, as well as Zn, Mg, Ga, In, etc., have been used to prepare different LDHs) and the divalent/trivalent molar ratio can be also changed within a rather broad range, as well as the interlayer anion (e.g., carbonate, chloride, nitrate, sulphate, polyoxometalates, anionic coordination compounds, etc.) [13–19]. We have previously reported on some of their applications in medicine as antacids and drug carriers [20], as anion scavengers [21,22], catalysts [23–26], catalyst supports and catalyst precursors [27–30].

We have also previously reported on the preparation of non-stoichiometric spinels containing Co and Fe [31], Ni, Co, Fe, and Al [32] and Ni and Fe [33] and we have studied their physicochemical properties and colour properties, specially analysing the changes arising from different molar ratios of the component cations. Studies have been also reported on the effect of doping by small amounts of a given cation for enhancing the colour [34], as well as the use of surfactants to obtain pigments with a narrow particle size distribution [35]. Systems containing other transition metal cations have been also studied [36–40]. One of the advantages of using LDHs as precursors for the pigment spinels is that we can modulate the properties of the calcined solids from the properties of the hydrotalcite-type precursors, and so such properties can be established beforehand. Preparation of Co-containing LDHs has been also described using microwaves as the heating medium, a method which permits a fine control of the particle size [41] and also avoids oxidation and formation of Co^{III} species [42]. The properties of LDHs and of the mixed oxides formed upon their calcinations when both Co and Cu exist in the interlayer, together with Al, strongly depend on the molar Cu/Co ratio [43].

In this paper, we present a comprehensive study of ceramic pigments prepared from LDH precursors containing cobalt and aluminum. It is well known that Co^{II} ions are responsible for the deep blue colour of ceramic pigments [1,44], because of their location in tetrahedral holes of the structure, where Laporte-partially allowed (by *d*–*p* mixing), spin-allowed transitions would occur, thus accounting for the intense colour observed. Such a location is observed in normal Co^{II}-containing spinels. On the other hand, it is also known that Zn^{II} cations behave as lattice modifiers, and consequently are able to tune very precisely the colour of the solid [45]. We have prepared two series of samples (without or with zinc), varying the divalent/trivalent molar ratio between 2/1 (stoichiometric LDH, leading to non-stoichiometric spinels) and 1/2 (non-stoichiometric LDH, leading to a stoichiometric spinel). The fact that Co^{II} species can undergo oxidation to the trivalent state and thus are able to substitute some of the Al^{III} cations from their positions, gives rise to interesting changes in the properties of these solids and consequently on their application as ceramic pigments. The samples prepared have been characterised using several physicochemical techniques and colour parameters ($L^*a^*b^*$) have been also determined.

2. Experimental

2.1. Sample preparation

All chemicals were from Panreac (PRS, puris.) and were used without any further purification. The samples were prepared by slow addition of a solution of the metal chlorides on a basic solution (NaOH and $NaHCO_3$), at room temperature. The total metal cations concentration was 2 M, the volume of the basic solution was twice that of the metal cations solution, and the HCO_3/Al molar ratio was fixed to unity. No insoluble residues were observed in the solutions before mixing.

Five samples with Co and Al were prepared, with nominal molar ratios (Co/Al) of 2/1, 3/2, 1/1, 2/3, and 1/2. For the five samples of the Zn, Co/Al system the same divalent/trivalent molar ratios were used, but with a Zn/Co molar ratio of 1/1 in all five cases.

Immediately after mixing the solutions, a pink precipitate was formed. Addition took 3–4 h, while the mixture was being mechanically stirred (400 ± 10 rpm, Heidolph mod. RZR-Z051 vertical stirrer). Stirring was continued during 14–20 h after addition was complete. The solids were then filtered in a Büchner funnel (20 cm diameter) with a water vacuum pump.

The mother liquids were colourless; this is not unexpected, as Al aquocomplexes are colourless and $[Co(H_2O)_6]^{2+}$ species display a weak pink colour. pH ranged between 9.3 and 9.9. Analysis showed the presence of a maximum of 0.16 ppm Co and 0.5 ppm Al for the Co/Al samples, but for the ternary samples the amount of Al was 1.11–2.19 ppm, while Zn was not detected and Co was between 0.19 and 0.30 ppm.

The dried solids were washed with four portions of 150 mL of distilled water each and a final portion of 500 mL. In each washing step the solid was maintained in contact with water for 30 min before connecting the water vacuum pump. Washing liquids were colourless and pH varied in the 9.3–10.1 range. Air was flowed through the cake for 2 h after the fifth washing step and the solid was then spread on a glass plate to dry at room temperature for 4–5 days, and then it was manually ground in an agate mortar.

Samples of the Co/Al system will be named as CoAl0*X*, where $X = 1$, 2, 3, 4, and 5 stand for the nominal Co/Al molar ratios of 2/1, 3/2, 1/1, 2/3, and 1/2, respectively. For the Zn,Co/Al system, samples will be named ZnCoAl0*X*, with the same meaning for *X*.

In order to prepare the mixed oxides, the samples were calcined up to 1200 °C at a heating rate of 5 °C/min, with a retention time of 5 h; after that the samples were let to cool freely. These calcined samples will be named as CoAl0*X*/1200 (or ZnCoAl0*X*/1200).

2.2. Characterisation

Element chemical analysis for metals was carried out at Servicio General de Análisis Químico Aplicado (University of Salamanca) by atomic absorption after dissolving the samples in nitric acid, in a Mark-II ELL-240 instrument. Carbon was analysed in a model CHNS-932 LECO elemental analyzer.

The powder X-ray diffraction (PXRD) patterns were obtained in a Siemens D-500 diffractometer using Cu Kα radiation ($\lambda = 1.5450$ Å) connected to a DACO-MP microprocessor using Diffract-AT software. The applied power was 1200 W (40 kV and 30 mA). The scan speed was 2° (2θ)/min, and the crystalline