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Intercalation of indigo carmine anions into zinc hydroxide salt: A novel alternative blue pigment

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ABSTRACT

Zinc layered hydroxide salt was intercalated with indigo carmine (IC) anions, transforming a soluble dye into an insoluble pigment. The obtained material was characterized by X ray powder diffraction, where a basal distance of 19.07 Å was obtained. DFT simulation showed that the groups of the indigo carmine are held by electrostatic and hydrogen bonds to water molecules positioned in the tetrahedral zinc apex. Fourier transform infrared and UV–Vis spectra confirmed that the intermolecular bonds are broken, and intramolecular bonds prevail in the intercalated compound. Thermal analysis curves (thermogravimetry – TGA and differential scanning calorimetry – DSC) showed that the intercalated IC is stable up to 350 °C and the mass loss is consistent with the expected compound formula ($Zn_5(OH)_8(IC)\cdot H_2O$). The obtained material presents layered crystals with micrometer sizes, as shown by scanning electron microscopy, and consists of a novel blue pigment mimicking the Maya blue pigment, having potential industrial applications.

1. Introduction

Synthetic azo dyes are by far the most widely used synthetic organic colored materials. These important compounds contain one or more azo groups (–N=N–) as part of their structure. They are widely applied as colorants in many industrial areas, such as cosmetics, inks, textiles, pharmaceutics, foods, plastics and leather, etc.

Due to their high solubility, in most applications organic azo dyes are dispersed and/or both chemically or physically bonded to the matrix. Their use is limited to compounds to which they have affinity. Due to low melting points, migration into the matrix, and poor affinity with the matrix, some dyes cannot be used as colorants in polymers.

Pigments are insoluble compounds and consequently can be used to color a wide range of substrates. That is the reason why the transformation of dyes into pigments is an alternative procedure to further expand the already wide application range of organic azo dyes. Although relatively laborious from the synthetic point of view, pigment lakes represent an important way to achieve such conversion [1,2] while another single step procedure is through intercalation into layered compounds [3–48].

To intercalate anionic species, two classes of synthetic compounds are available: layered double hydroxides (LDHs) and layered hydroxide salts (LHSs). LDH structures are based on the mineral Brucite, where Mg^{+2} cations are octahedrally coordinated by six hydroxyl anions. The octahedrons are connected at their corners, building regular "two-dimensional" layers that are stacked along the basal axis. In LDH, part of the octahedral Mg^{+2} is substituted by M^{+3} cations, generating an excess of positive charge which is compensated by the intercalation of hydrated anions. The general LDH formula is $M^{+2}{}_{1-x}M^{+3}{}_x(OH)_2(A^{-n})_{x/n}\cdot yH_2O$.

In LHS, the excess of positive charge is obtained when some of the hydroxyl anions are removed from the structure and compensated by intercalated hydrated anions. The general LHS formula is $M^{+2}(OH)_{2-x}(A^{-n})_{x/n}\cdot yH_2O$ [10].

The intercalation/adsorption of anionic dyes into/onto layered materials is frequently described in the literature, but the number of studies is smaller for blue dyes [3,6,7,13,16,18,19,22,46]. Most of the compounds used as matrixes are LDH, while only a small number of papers report the use of LHS for this same purpose [19,26,46].

Although not part of the azo dye family, indigo dyes are the oldest and most important dyes, used mainly by the textile industry

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in the dyeing of cotton and wool fabrics [49]. To improve water solubility, indigo dye is sulfonated and transformed into a disodium salt (indigo carmine).

After immobilization of indigo carmine anions into layered compounds, the obtained blue pigment mimics Maya blue, a sky-blue color pigment which was used for many purposes as a durable colorant during pre-Columbian times in the Yucatan Peninsula in Mexico [50]. Maya blue was obtained when a magnesium and aluminum fibrous phyllosilicate (Palygorskite, ideal formula $Mg_2Al_2Si_8O_{20}(OH)_2(H_2O)_4 \cdot 4H_2O$) mixture was heated and crushed with leaves of *Indigofera suffruticosa*, *Indigofera tinctoria* or *Isatis tinctoria*, plants that release the indigo dye. Other components were also sometimes included in the mixture, but the fundamental formulation generated a hybrid material that could withstand centuries of harsh weather conditions, even when treated with solvents, alkaline or acid aqueous solutions [51,52].

Due to the lack of information in the literature regarding the intercalation of indigo dyes into LHS matrixes, the objective of this paper is to report the synthesis, characterization and application of a blue pigment obtained by the intercalation of indigo carmine anions into the layered zinc hydroxide salt structure. This procedure not only intercalates the individual anions between the layers, avoiding their migration, but also improves their thermal, photo and chemical stability [12,22,28,31].

2. Materials and methods

2.1. Synthesis

Disodium salt of indigo carmine (Na_2IC) (acid blue 74, Color index 73015) $C_{16}H_8N_2Na_2O_8S_2$ = [3,3′-dioxo-1,3,1′,3′-tetrahydro-[2,2′]-bi-indolylidene-5,5′-disulfonic acid disodium salt], analytical grade (>99%), was purchased from Acros Organics company.

Intercalation of indigo carmine anions (IC) into a layered zinc hydroxide salt (IC/LHS) was achieved by co-precipitation at constant pH, where 100 mL of $ZnCl_2$ 0.167 mol/L (Vetec 97%) (solution A) and NaOH 0.333 mol/L (Vetec 99%) (solution B) were simultaneously dropwise added to 100 mL of the solution of Na_2IC in the molar concentration of 0.04 mol/L.

During reaction the solution was magnetically stirred, the pH controlled close to neutrality and the final solution/dispersion pH was fixed at 7.8. The mixture was magnetically stirred for 24 h at room temperature, after which the solid was separated by centrifugation at 4000 rpm followed by five washing/dispersion steps and final drying under vacuum at 60 °C for 24 h.

To investigate the structure of IC/LHS after dehydration, part of the sample was deposited in a glass Petri dish and heated at 200 °C in a muffle oven for 30 min under static air atmosphere.

2.2. Instrumental analysis

X-ray powder diffraction spectra (XRD) were obtained by depositing the materials onto glass sample holders and analyzing them with a Shimadzu XRD-6000 diffractometer with a dwell time of 2° min^{-1} and step of 0.02°. The source radiation was provided by a Cu cathode (K_α = 1.5418 Å), to which were applied a current of 30 mA and voltage of 40 kV.

Fourier-transform infrared measurements (FTIR) were obtained in transmission mode with a Bio-Rad FTS 3500GX spectrometer. The samples (around 1% by mass) were gently crushed with KBr, pressed into pellets at 6.5 tons and the spectra were obtained by accumulation of 32 scans, in the range of 4000–400 cm^{-1} and resolution of 4 cm^{-1}.

UV–Visible spectra were collected with a PerkinElmer Lambda 1050 spectrophotometer. A small amount of each sample was milled with analytical grade glycerol and the spectra were collected by transmission mode in the range of 200–800 nm.

Simultaneous thermal analysis (thermogravimetry – TGA and differential scanning calorimetry – DSC) was carried out in a Netzsch STA 449 F3 Jupiter analyzer using alumina crucibles. Measurements were performed in flowing synthetic air (50 mL L^{-1}) at a heating rate of 10 °C min^{-1}.

Scanning electron microscopic (SEM) images and qualitative elemental analysis (energy dispersive X-ray spectroscopy - EDS) spectra were obtained with a Tescan Vega 3 LMU scanning electron microscope. The samples were deposited on aluminum stubs and submitted to analysis at low vacuum and with voltage of 10 kV.

2.3. Computational details

In order to simulate the anion intercalation between the $[Zn_5(OH)_8 \cdot 2H_2O]^{2+}$ layers and to reduce the computational costs, the primitive cell of the layered hydroxide salt, described elsewhere [53], was used with the following lattice parameters: v_1 = (a/2, 0.16a, 0), v_2 = (−0.06b, 0, 0.99b), v_3 = (0, c, 0), where a, b and c are the lattice parameters of the crystallographic unit cell. The *ab initio* calculations were performed using the codes available in the Quantum Espresso package [54], which implements the Density Functional Theory [55,56] with periodic boundary conditions. The Generalized Gradient Approximation (GGA/PBE) [57] was used for the exchange-correlation functional and the ion cores were described by Vanderbilt ultrasoft pseudopotentials [58]. The Kohn–Sham electron states were expanded in a plane wave basis set with a kinetic cutoff energy of 60 Ry (600 Ry for the density). Monkhorst-Pack meshes of 3 × 3 × 1 k-point sampling in the first Brillouin zone were also used [59]. The structure was fully optimized by minimizing the total energy gradient until all the force components were lower than 0.001 Ry/Bohr.

After optimization of the hydrated structure, the water molecules grafted to the zinc tetrahedra were removed and the structure was fully optimized.

Charge density difference plots were also made to evaluate interactions between the hydroxide salt layer and the anion for the hydrated and dehydrated structure. The following equation represents the charge density difference:

$$\rho_{diff} = \rho_{total} - \rho_{layer} - \rho_{anion}$$

where ρ_{diff}, ρ_{total}, ρ_{layer}, ρ_{anion} represent, respectively, the charge density difference, the charge density of the whole system, the charge density of the layer and the charge density of the anion. The contour spacing of the plots was 0.003 electrons/$Bohr^3$. The molecular graphics and the density plots were generated by the XCrySDen graphical package [60].

3. Results and discussion

The X-ray diffraction pattern of IC/LHS shows a series of basal peaks (indicated by the indexation 001 in Fig. 1) and a basal distance of 19.07 Å was obtained from the higher order diffraction basal peak (005).

This value is lower than those found in IC intercalated into Mg/Al layered double hydroxide (LDH) using a molar ratio of 2:1 (21.3 Å) [18] and Mg:Al LDH in a molar ratio of 3:1 (between 21.2 and 22.2 Å, considering direct synthesis or anionic exchange) [3] and higher than those obtained by the direct co-precipitation of Zn:Al LDH in a molar ratio of 2:1 (17.6 Å) [61].

Our new material has a structure which is probably similar to $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$, as non-basal peaks of this compound are also observed (indicated by asterisks). Although the IC anion length