



Preparation and Characterization of Cu(II) Phthalocyanine Tetrasulfonate Intercalated and Supported on Layered Double Hydroxides

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Abstract

The aim of the present work was to synthesize and characterize layered double hydroxides (LDHs), in the magnesium/aluminum form, intercalated with copper(II) phthalocyanine tetrasulfonate (CuPcTs). The metal complex was immobilized into the LDH gallery region through the reconstitution method and this material was characterized by X-ray diffraction (XRD), surface area and porosity measurements, elementary analysis, thermogravimetry (TGA), vibrational (IR) and electronic (UV-visible) spectroscopies, and electronic paramagnetic resonance (EPR). The catalytic performance of CuPcTs intercalated and supported on the LDH was evaluated by carrying out the hydrogen peroxide dismutation. The CuPcTs was successfully intercalated into the LDH layers according to XRD data (the basal spacing of the carbonate precursors increases by approximately 15 Å in the intercalated samples). The surface area and porosity analysis suggested that the CuPcTs intercalated materials are not microporous solids. Samples containing the metal complex confined between the LDH layers have an appreciable thermal stability: decomposition is not observed at least up to 400 °C. TGA experiments also show that the weight-loss curves of the CuPcTs supported samples superimpose those recorded for the CuPcTs complex and the LDH-carbonate while the curves for the intercalated materials are unique. CuPcTs intercalated or supported on LDHs is not active in the hydrogen peroxide dismutation although the free form shows activity at pH above 8.

Introduction

Intercalation of guest species as metal complexes and organic molecules into two or three-dimensional inorganic matrices can be seen as a versatile synthetic method for the preparation of systems organized at nanoscale level [1]. Studies involving photo- [2] and catalytic processes [3] in restricted media have shown the interesting physical and chemical properties arising from the guest–host interactions in these nanostructured materials.

Considering the utilization of the intracrystalline matrix region as a micro reactor to achieve selective chemical reactions, some studies were reported about the intercalation of synthetic biomimetic models such as porphyrins, phthalocyanines and Schiff bases metal complexes in zeolites and layered inorganic structures [4]. Among two-dimensional matrices, layered double hydroxides (also denominated anionic clays) intercalated with metal complexes containing macrocyclic ligands have been quoted as an interesting system to be evaluated for catalytic purposes [5].

Layered double hydroxide (LDHs) composition can be represented by the general formula $[M_{(1-x)}^{II}M_x^{III}(\text{OH})_2] \times (\text{A}^{n-})_{x/n} \cdot z\text{H}_2\text{O}$, where A^{n-} is the interlayer anion; $M^{II} = \text{Mg, Mn, Fe, Co, Ni, Cu, Zn}$ and Ca ; $M^{III} = \text{Al, Cr, Mn, Fe, Co, Ni}$ and La [5]. The layer structure is similar to that observed to brucite: the cations are localized in the octahedral sites of $\text{M}(\text{OH})_6$ units joined by the edges. The hydrated anions that neutralize the positive layer charge occupy the region between the layers (Figure 1a). Taking into account the nature of $M_{II/III}$ and A^{n-} , and the cation molar ratio, it is possible to synthesize LDHs of several compositions. Details about the LDH structure, preparation and application in a variety of fields as, for example, catalysis, advanced ceramics and pharmacology have been reviewed in the literature [5–7].

Studies about the isolation and characterization of LDHs intercalated with anionic (sulfonated or carboxylated) porphyrins and phthalocyanines, in particular, have focused on non-metallated macrocycles [8–10] and the metal derivatives of cobalt [10–19], copper [16, 17, 20–22], manganese [23], nickel [19, 24] and zinc [17, 25]. In several works, these LDH materials were prepared in the magnesium/aluminum

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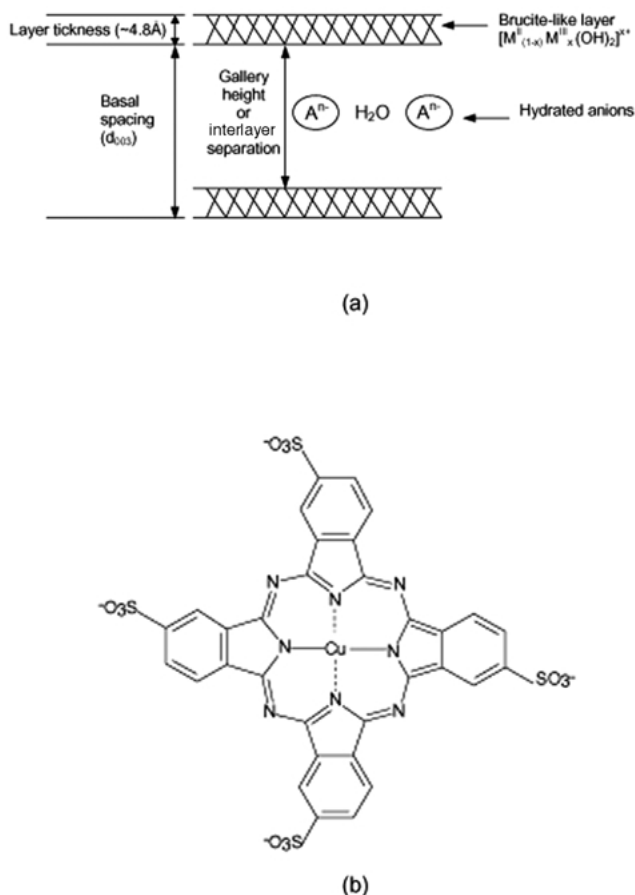


Figure 1. (a) Schematic representation of a layered double hydroxide structure and (b) Cu(II) phthalocyanine tetrasulfonate (CuPcTs).

form (Mg/Al molar ratio in the range 2-4) [8, 10, 11–17, 19–21, 23] through the following synthetic approaches: (i) coprecipitation of the layer M^{II}/M^{III} cations in the presence of the macrocycle, (ii) anion exchange reaction and (iii) reconstitution method in which a calcined LDH is used as precursor.

The majority of authors has attributed a perpendicular or tilt orientation for the conjugated ring of the macrocycle (porphyrins and phthalocyanines) relative to the LDH layers, according to the basal spacing value obtained by X-ray diffraction data. The high layer charge density of LDHs compared to the smectite clays seems to guide the macrocycle arrangement between the layers, favoring the exposition of the metal center and promoting catalytic conversions. In this way, catalytic studies of thiols [11, 16–17] and 2,6-di-tert-butyl phenol [12, 15] oxidation and the reductive dehalogenation of carbon tetrachloride [14] were conducted employing LDH immobilized anionic Co(II) phthalocyanines. Another work includes the conversion of cyclohexanol to cyclohexanone, using H_2O_2 as oxidant in the presence of sulfonated Cu(II) phthalocyanine intercalated into LDH [21]. Oxidation of cyclohexene over a LDH intercalated with Co(II) phthalocyanine tetrasulfonate (CoPcTs) was monitored *in situ* by XRD (X-ray diffraction) and EXAFS (X-ray absorption fine structure spectroscopy) [18]. Recently a review was published about the LDH systems intercalated with metal

complexes and oxometalates comprising macrocyclic ligand complexes [26].

In the reported studies about the reactivity of LDH intercalated materials, the catalytic activity, selectivity and macrocycle stability have been evaluated considering the textural characteristics of the LDHs (basal spacing and surface area), the degree of macrocycle aggregation, the hydrophilic/hydrophobic nature of the host layers and the substrates, the possible electronic configuration modification due to confinement, and the deactivated forms of the catalyst. All these parameters are recognized as very important in the catalytic data analysis but, unfortunately, in some cases, the intercalated material characterization is not sufficient to permit a more accurate interpretation of the catalytic behavior or even the comparison between similar LDH systems.

We have prepared samples containing copper phthalocyanine complex (Figure 1b) immobilized on layered double hydroxides through two synthetic routes: (i) guest species were intercalated between the LDH layers by the reconstitution method; (ii) guest species were supported on the external surfaces of LDHs. Textural and spectroscopic properties of these solid samples were evaluated and contrasted. Additionally we have investigated the performance of the free and immobilized complexes in the hydrogen peroxide decomposition in order to better elucidate the CuPcTs arrangement in the inorganic layered matrix.

Experimental

Synthesis of LDHs intercalated by carbonate ions

The layered precursors containing carbonate ions and a Mg^{2+}/Al^{3+} molar ratio of 3 and 4 (abbreviated as $Mg_3Al-CO_3^{2-}$ and $Mg_4Al-CO_3^{2-}$, respectively) were prepared by the coprecipitation procedure as described by Miyata [27]. $Mg_3Al-CO_3^{2-}$ was synthesized as follows: a mixture of $Mg(NO_3)_2 \cdot 6H_2O$ (20.002 g, 78 mmol) and $Al(NO_3)_3 \cdot 9H_2O$ (9.756 g, 26 mmol) was dissolved in ca. 100 mL of deionized water. The aqueous solution was added under stirring to approximately 150 mL of Na_2CO_3 solution at pH 10. The pH was maintained at 10 by continuous addition of 0.2 mol/L Na_2CO_3 (molar ratio $CO_3^{2-}/Al^{3+} = 0.7$) and, subsequently, of 2 mol/L NaOH aqueous solution. The precipitate was maintained in suspension at 80 °C for 12 h. The solid was isolated by centrifugation and rinsed with an 0.1 mol/L Na_2CO_3 ($CO_3^{2-}/Al^{3+} = 0.5$) aqueous solution. Washing steps were performed with deionized water until peptization of the solid. The LDH containing carbonate was dried at 80 °C for 48 h. $Mg_4Al-CO_3^{2-}$ was prepared as described above but starting with a mixture of $Mg(NO_3)_2 \cdot 6H_2O$ (20.002 g, 78 mmol) and $Al(NO_3)_3 \cdot 9H_2O$ (7.323 g, 19.5 mmol).

Synthesis of Cu(II) phthalocyanine tetrasulfonate intercalated into LDHs by the reconstitution method

Copper(II) 3,4',4'',4'''-phthalocyaninetetrasulfonate (CuPcTs, tetrasodium salt, 85%, Aldrich) was used as re-

ceived and submitted to elemental and thermogravimetric analysis. Found: C, 31.3%; H, 3.0%; N, 9.7%; Cu, 5.4%; H₂O, 11.5%. These results indicated that the macrocycle sample contains about 83% of CuPcTs as previously stated by the supplier.

Approximately 1 g of the Mg₃Al-CO₃²⁻ and Mg₄Al-CO₃²⁻ samples were calcined at 500 °C for 4h under air. The mixed metal oxide formed by the thermal decomposition of the LDHs was suspended in 100 mL of deionized and decarbonated water and stirred at room temperature for 15 h under a static nitrogen atmosphere. A CuPcTs solution was prepared using deionized and decarbonated water and added to the suspensions containing the rehydrated LDHs. The final CuPcTs solution was about 4 mmol/L and the molar ratio CuPcTs/Al³⁺ ~ 0.5. The systems were stirred under nitrogen flow at 100 °C for 12 h. The intercalated solids were isolated by centrifuging and washed with deionized and decarbonated water until the observation of a colorless supernatant. The solid samples were dried in a desiccator under vacuum by using silica gel as drying agent. The two LDHs intercalated by the reconstitution method were abbreviated as Mg₃Al-(CuPcTs)_{int} and Mg₄Al-(CuPcTs)_{int}.

Synthesis of Cu(II) phthalocyanine tetrasulfonate supported on LDH carbonate

Mg₃Al-CO₃²⁻ and Mg₄Al-CO₃²⁻ containing supported CuPcTs were prepared suspending 1 g of LDH in 150 mL of about 4 mmol/L macrocycle solution (molar ratio CuPcTs/Al³⁺ ~ 0.5). The suspensions were maintained under stirring at 80 °C for ca. 45 h. The samples were washed and dried as described for the intercalated materials. The two LDH-CO₃²⁻ containing the copper complex supported on the external surface were abbreviated as Mg₃Al-(CuPcTs)_{sup} and Mg₄Al-(CuPcTs)_{sup}.

Instrumental

Elemental analysis (C, H, N) were carried out using a Perkin Elmer model 2400 analyser. LDH samples were dissolved in 1% (v/v) nitric acid solution and the metal amounts were determined by ICP emission spectroscopy on a Spectro Analytical Instruments spectrometer.

X-ray diffraction (XRD) patterns of powder and oriented films were recorded on a Philips diffractometer model PW1710 or model X'PERT-MPD using CuK_α radiation (40 kV and 40 mA), a step of 0.02° and an accumulation time of 1 s/step.

Thermogravimetric analysis (TGA) was conducted on a Shimadzu TGA-50 instrument under synthetic air (flow rate = 50 mL/min) using a heating rate of 10 °C/min up to 900 °C. The Mg₃Al-(CuPcTs)_{int} sample was also heated in a Shimadzu TGA-50H instrument up to 1200 °C under air.

Specific area (BET-N₂ method) was determined on a Quantachrome model Quantasorb sorption system after heating the samples at 200 °C for 2 h under nitrogen gas flow. Specific area and porosity analysis of Mg₃Al-(CuPcTs)_{int} and Mg₄Al-(CuPcTs)_{int} were determined from N₂ adsorption-desorption isotherms at liquid nitrogen tem-

perature using a Micromeritics Asap 2010 instrument and associated software. Samples for sorption analysis were heated at 200 °C for 2 h under vacuum.

FT-IR spectra of samples in KBr matrix were recorded on a MIDAC model PRS-INT series 192 spectrometer and on a Perkin Elmer model 1750 spectrometer, in the range 4000–400 cm⁻¹.

Electronic absorption UV-visible spectra of CuPcTs aqueous solutions were recorded in a Hitachi model U-2000 spectrophotometer. A Shimadzu model UV-2401PC spectrophotometer equipped with an integration sphere was employed to record the diffuse reflectance spectra (BaSO₄ from Waco Pure Chem. was used to dilute the solid samples).

EPR experiments were conducted in a Bruker EMX spectrometer (or a Bruker ER 200D-SRC instrument), operating at X-band (ca. 9.5 GHz), and using DPPH (α,α' -diphenyl- β -picryl hydrazyl) for calibration. Instrumental standard conditions for the measurements were: frequency = 9.48 GHz, microwave power = 20 mW, modulation frequency = 100 kHz, modulation amplitude = 2 G, at liquid nitrogen temperature (77 K), or at room temperature (298 K).

Hydrogen peroxide dismutation

The catalase-like activity of CuPcTs at homogeneous and heterogeneous (intercalated and supported on LDHs) conditions was evaluated by monitoring the released molecular oxygen, employing a Warburg apparatus, from B. Brown, model V-85, at a constant temperature of (30.0 ± 0.1)°C, and shaking of 120 strokes/min. Solutions of hydrogen peroxide were prepared by adequate dilution of a 35% commercial reagent (from Peroxidos de Brasil Ltda.), free from stabilizers. Analyses of the peroxide solutions were performed by a modified vanadate method [28]. The reactions were performed in borate buffered solutions (pH 7.99 and 9.59). Each experiment was conducted at least in duplicate, by adding the complex aqueous solution (0.30 mL, 25 mmol/L solution) or the solid samples (10–70 mg) to the sidearm, and the peroxide solutions (2.70 mL, 6.16 mmol/L solution) to the main compartment of the Warburg flasks. In a typical experiment 0.30 mL of 25 mmol/L CuPcTs aqueous solution, 12 mg of Mg₄Al-CO₃²⁻, 21 mg of Mg₄Al-(CuPcTs)_{int}, and 68 mg of Mg₄Al-(CuPcTs)_{sup} (the amount of Cu(II) was the same in the homogeneous and heterogeneous experiments) were used. To the recipients containing the solids, 2.70 mL of buffered solution was also added to complete the 3.00 mL total volume. The reaction was started by mixing the sidearm and main recipient contents. Control experiments, without adding any catalyst, showed negligible decomposition of the peroxide in the same experimental conditions.

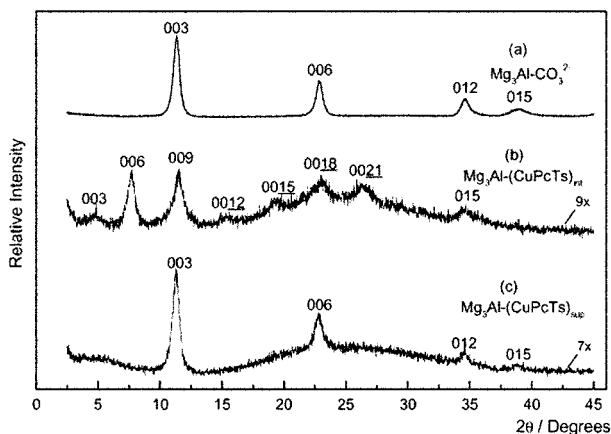


Figure 2. XRD patterns of (a) $\text{Mg}_3\text{Al-CO}_3^{2-}$; (b) $\text{Mg}_3\text{Al-(CuPcTs)}_{\text{int}}$ and (c) $\text{Mg}_3\text{Al-(CuPcTs)}_{\text{sup}}$.

Results and discussion

CuPcTs intercalated and supported on LDHs

Taking into account the elemental analysis (C, H, Mg and Al) and TGA data (water content) shown in Table 1, the following compositions can be proposed for the LDH samples used as precursors for the macrocycle intercalation: $[\text{Mg}_{4.21}\text{Al}(\text{OH})_{10.42}](\text{CO}_3)_{0.5.3.71} \text{H}_2\text{O}$ and $[\text{Mg}_{3.03}\text{Al}(\text{OH})_{8.06}](\text{CO}_3)_{0.5.3.17} \text{H}_2\text{O}$.

Considering the molar ratio $\text{Mg}^{2+}/\text{Al}^{3+}$ (see Table 1), one can infer that the CuPcTs insertion into LDHs by the reconstitution method decreases the layer charge density of the brucite-like layers when compared to the charge density of the precursors $\text{Mg}_3\text{Al-CO}_3^{2-}$ and $\text{Mg}_4\text{Al-CO}_3^{2-}$ (we are considering here that the layer charge density is related to the Al^{3+} amount). The molar ratio $\text{Al}^{3+}/\text{CuPcTs}$ for the two intercalated samples is very close to that expected for materials where the positive layer charges are practically 100% neutralized by the tetrasulfonated metallophthalocyanine.

XRD patterns recorded for the Mg_3Al and Mg_4Al systems (Figures 2 and 3, respectively) confirm the CuPcTs intercalation via the reconstitution method. The basal spacing of LDH-carbonate samples increases considerably after the macrocycle incorporation (see Table 2).

The $00l$ reflections peaks observed for $\text{Mg}_3\text{Al-(CuPcTs)}_{\text{int}}$ and $\text{Mg}_4\text{Al-(CuPcTs)}_{\text{int}}$ are in agreement with those reported by Carrado *et al.* [20] for samples containing CuPcTs intercalated in a hydrotalcite-like material ($\text{Mg}^{2+}/\text{Al}^{3+} = 3$) through the ion exchange reaction (LDH-nitrate as precursor) and through the coprecipitation method at pH 10.5. Although the basal spacing obtained for the isolated samples is equal ($d_{003} = 23 \text{ \AA}$), the authors observed that the relation of intensities of harmonic $00l$ peaks was altered depending on the procedure used to prepare the samples. In the present study, the XRD patterns of LDH-immobilized metallophthalocyanine show a 003 peak of low intensity if compared to the 006 and 009 peaks.

Kannan *et al.* [21] have also prepared the CuPcTs complex intercalated into magnesium-aluminum LDHs ($\text{Mg}^{2+}/\text{Al}^{3+} = 2, 3$ and 4) by coprecipitation at pH 10.

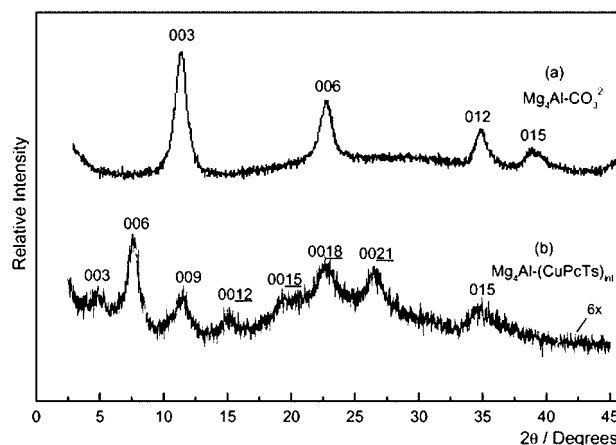


Figure 3. XRD patterns of (a) $\text{Mg}_4\text{Al-CO}_3^{2-}$ and (b) $\text{Mg}_4\text{Al-(CuPcTs)}_{\text{int}}$.

XRD patterns of the three isolated samples exhibited a basal spacing (d_{003}) of 12.8–13.0 \AA attributed to a macrocycle intercalated phase and some diffraction peaks related to a LDH-nitrate phase. The isolation of mixture phases for metallophthalocyanine-LDH systems can be related to the CuPcTs/ Al^{3+} molar ratio employed in the synthesis. According to some reports in the literature [12, 20] and our observations, to obtain pure phases it is necessary to use an excess of metallophthalocyanine relative to the amount needed to neutralize the layer charge. CuPcTs intercalated material was also prepared by Iliev *et al.* [16] through the reconstitution method using a magnesium-aluminum LDH ($\text{Mg}^{2+}/\text{Al}^{3+} = 2.5$) but unfortunately characterization data such as elemental analysis and XRD were not reported.

A basal spacing of *ca.* 23 \AA (or a gallery height of 18.2 \AA if the layer thickness is considered) have been observed for various phthalocyanines confined between LDH layers [10–12, 15, 18, 20] and ascribed to a perpendicular orientation of the macrocycle ring relative to the brucite-like layers.

In the present work, samples containing CuPcTs supported on LDHs were also prepared with the purpose of distinguish the catalytic role of the complex in different matrix sites (intercalated between internal surface or supported on the external surface). As shown in Figure 2, the XRD of the $\text{Mg}_3\text{Al-(CuPcTs)}_{\text{sup}}$ sample is similar to that of the carbonate precursor considering that only CO_3^{2-} ions occupy the gallery region (the metallophthalocyanine intercalation in a flat orientation is precluded owing to the fact that the basal spacing expected for this arrangement should be higher than 8 \AA). Both the supported samples have practically the same CuPcTs content (see Table 1) and similar BET surface area (see Table 2) evidencing once again the presence of the metallophthalocyanine not between the layers but on the LDH external surface (basal surface and edges, probably).

Thermal analysis

The thermal stability of isolated LDH samples was verified by thermogravimetric analysis. Considering the possible utilization of LDH-metallophthalocyanines systems in heterogeneous catalysis, the thermal behavior of these materials

Table 1. Elemental analysis and thermogravimetric data of synthesized layered materials

| Sample ^a | Non-metal analysis | | | C:N ^b molar relation | Mg:Al:Cu molar relation | mmol Cu/g of LDH | % H ₂ O (weight) |
|--|--------------------|-----|-----|------------------------------------|----------------------------|---------------------|--------------------------------|
| | %C | %N | %H | | | | |
| Mg ₃ Al-CO ₃ ²⁻ | 2.3 | – | 3.9 | – | 3.03:1 | – | 17.6 |
| Mg ₄ Al-CO ₃ ²⁻ | 1.8 | – | 3.6 | – | 4.21:1 | – | 16.6 |
| Mg ₃ Al-(CuPcTs) _{int} | 18.2 | 4.6 | 3.3 | 4.6:1 | 3.28:1:0.24 | 0.42 | 11.9 |
| Mg ₄ Al-(CuPcTs) _{int} | 14.8 | 4.0 | 3.3 | 4.3:1 | 4.38:1:0.28 | 0.39 | 14.1 |
| Mg ₃ Al-(CuPcTs) _{sup} | 6.7 | 1.4 | 3.8 | 5.6:1 | | 0.15 ^c | 15.7 |
| Mg ₄ Al-(CuPcTs) _{sup} | 6.0 | 1.3 | 3.7 | 5.4:1 | | 0.12 ^c | 17.0 |

^aAbbreviations are indicated in the text.

^b CuPcTs expected C/N molar ratio = 4.

^c Cu amount was calculated through the nitrogen amount considering the molar relation 1:8.

Table 2. XRD and specific area (BET-N₂) data of the synthesized layered materials

| Sample | d/Å (h k l) | | | | | Specific area m ² /g |
|--|----------------|-------|-------|--------|--------|------------------------------------|
| Mg ₃ Al-CO ₃ ²⁻ | 8.0 | 3.9 | 2.6 | 2.3 | | 86.4 |
| | (003) | (006) | (012) | (015) | | |
| Mg ₄ Al-CO ₃ ²⁻ | 8.1 | 4.0 | 2.6 | 2.3 | | 109.8 |
| | (003) | (006) | (012) | (015) | | |
| Mg ₃ Al-(CuPcTs) _{int} | ~23 | 11.5 | 7.7 | 5.7 | 4.6 | 67.5 |
| | (003) | (006) | (009) | (0012) | (0015) | |
| Mg ₄ Al-(CuPcTs) _{int} | ~23 | 11.5 | 7.7 | 5.9 | 4.6 | 26.0 |
| | (003) | (006) | (009) | (0012) | (0015) | |
| Mg ₃ Al-(CuPcTs) _{sup} | (a) | | | | | 79.5 |
| Mg ₄ Al-(CuPcTs) _{sup} | (a) | | | | | 82.9 |

(a) The diffraction pattern is similar to that observed for the related LDH-carbonate.

is an important parameter to be evaluated. Also the LDH-metal complexes can be used as precursors to get mixed oxides catalysts after thermal decomposition. As it will be shown, the localization of the guest species (intercalated or supported) can lead to distinct decomposition products. Figure 4 shows the recorded curves of weight loss for the Mg₃Al systems. For comparison purposes, the TGA curve for CuPcTs (sodium salt) is also included.

CuPcTs loses hydration water up to *ca.* 180–200 °C and decomposes above 450 °C. The decomposition step seems to include two stages up to 600 °C. The IR vibrational spectrum of the CuPcTs sample obtained at 900 °C (a gray powder) does not show bands related to the macrocycle organic skeleton and the spectral profile can be assigned to anhydrous Na₂SO₄ [29]. The peaks observed at 1120 and 620 cm⁻¹ are attributed to the ν₃ and ν₄ modes of the sulfate ion respectively [30]. Also a weak band at 992 cm⁻¹ is present and it can be related to the sulfate ν₁ IR inactive mode, suggesting a lowering of symmetry from tetrahedral. Taking into account the vibrational spectroscopic data, we can propose that the product isolated at 900 °C is a mixture of CuO and Na₂SO₄. The slight weight loss above *ca.* 750 °C (see Figure 4a) may be due to the sodium sulfate decomposition to SO₃. Figure 4b shows the TGA curve for the LDH carbonate. The first step of weight loss (up to 210 °C) is ascribed to the water release and the second one (above 300 °C) to the LDH

dehydroxylation and decarbonation as discussed previously [31].

The Mg₃Al-(CuPcTs)_{sup} thermal behavior is very interesting (see Figure 4c) and it can be interpreted as the overlap of curves *a* (CuPcTs decomposition) and *b* (LDH carbonate decomposition). We have also observed this feature for Mg₄Al-(CuPcTs)_{sup} and other magnesium-aluminum LDH systems containing CoPcTs supported on the matrix external surface. It is important to note that the weight loss at *ca.* 550 °C observed for CuPcTs (Figure 4a) is not observed for the LDH supported sample (Figure 4c). Also it is observed that the solid isolated at 900 °C has a light green coloration. The IR vibrational spectrum of Mg₃Al-(CuPcTs)_{sup} heated at 900 °C shows bands at 1120 and 620 cm⁻¹ assigned to sulfate ion (further information see below).

The TGA curve for the Mg₃Al-(CuPcTs)_{int} sample is different from that recorded for the supported sample. Figure 4d reveals that the CuPcTs intercalated sample is stable at least up to 400 °C which is a very interesting result for catalytic purposes in the solid-gas phase. We have observed similar thermal stability for a magnesium-aluminum LDH intercalated with CoPcTs. The CuPcTs intercalated sample heated at 900 °C is yellow and its IR spectrum indicates the presence of sulfate ion in a C_{3v} symmetry as characterized by the bands at 1150 and 1096 cm⁻¹ (splitting of the degenerate ν₃ mode), 988 and 628 cm⁻¹. Some weak bands (*ca.* 1288, 920 and 712 cm⁻¹) are also observed. Considering the

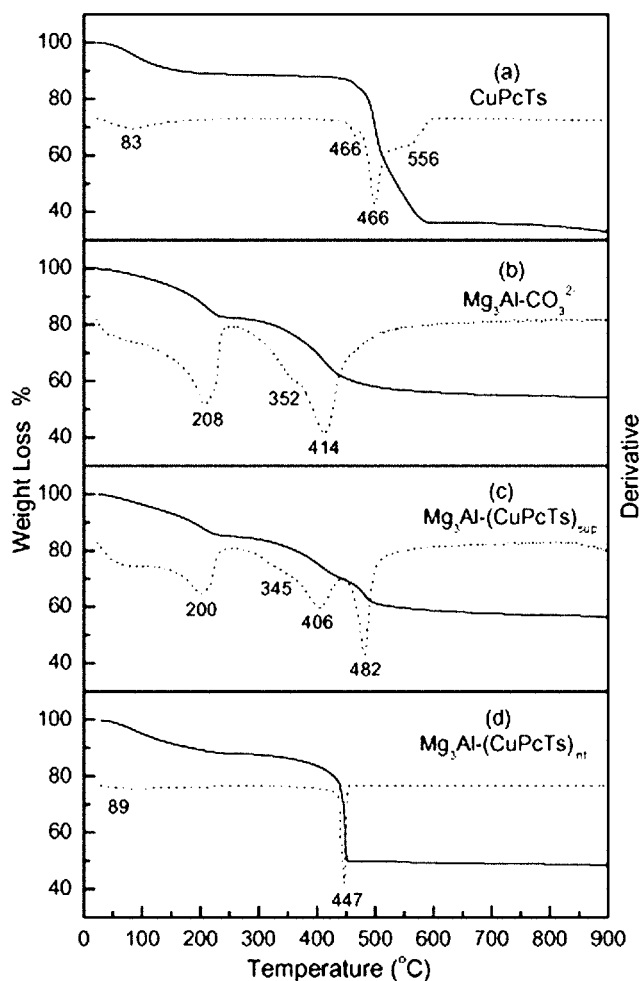


Figure 4. TGA (solid line) and DTG (dashed line) curves for (a) CuPcTs (sodium salt); (b) $\text{Mg}_3\text{Al}-\text{CO}_3^{2-}$; (c) $\text{Mg}_3\text{Al}-(\text{CuPcTs})_{\text{sup}}$ and (d) $\text{Mg}_3\text{Al}-(\text{CuPcTs})_{\text{int}}$.

colors observed for the supported and intercalated samples heated at 900 °C we can say that the decomposed LDH structure is providing the copper ion stabilization as a phase distinct of CuO. We tried to identify the products formed after decomposition at 900 °C by XRD but the recorded patterns show poor crystallized phases and only the MgO and MgAl_2O_4 peaks could be definitely attributed. To improve the XRD patterns, the samples were calcined at 900 °C for 4 h under air. Once again it was not possible to identify other phases besides those above mentioned. Comparing to the CuPcTs intercalated and supported samples heated at 900 °C, after isothermal treatment at this temperature for 4 h, samples show the same color and the sulfate ion bands are present in their IR spectra (for the intercalated sample, the bands at 1286, 916 and 717 cm^{-1} were intensified).

The TGA curve for the $\text{Mg}_3\text{Al}-(\text{CuPcTs})_{\text{int}}$ sample recorded up to 1200 °C (not shown) shows that the solid loses about 7.5% of weight in the range 700–1200 °C. The material isolated at 1200 °C is pale yellow and its IR spectrum does not show bands related to the sulfate ion. Moreover, peaks at 1002, 906 and 706 cm^{-1} are observed, which cannot be attributed to any usual oxo-ion of sulfur.

We have proposed that the magnesium–aluminum LDH containing intercalated sulfate ions undergoes a grafting reaction when heated above 250 °C (anhydrous material) [31]. The $\text{Mg}_3\text{Al}-(\text{CuPcTs})_{\text{int}}$ sample was heated at 200 °C under vacuum until a constant pressure value was observed. After the dehydration treatment, the $\text{Mg}_3\text{Al}-(\text{CuPcTs})_{\text{int}}$ XRD pattern did not change (a basal spacing contraction is not observed) suggesting that the grafting of the phthalocyanine sulfonic groups is not occurring. Therefore the thermal stability of the brucite-like layers in the $\text{Mg}_3\text{Al}-(\text{CuPcTs})_{\text{int}}$ cannot be attributed to a formation of crosslinked CuPcTs between the layers.

Concerning the characterization of phthalocyanine-LDH compounds by thermal analysis, only one article has been found reporting their thermal behavior. Kannan *et al.* [21] have performed TGA experiments on the CuPcTs complex and an intercalated Mg_3Al -LDH material under nitrogen atmosphere up to 700 °C. The TGA and DTG curves for the CuPcTs are similar to those shown in Figure 4a. However, under nitrogen atmosphere, the DTG peaks for the decomposition steps are observed at higher temperatures. According to the authors, the CuPcTs–LDH isolated compound is a mixture of two phases as mentioned above. In view of the distinct composition of this compound compared to the $\text{Mg}_3\text{Al}-(\text{CuPcTs})_{\text{int}}$ sample and also the different atmosphere used in the TGA experiments, data comparison is impracticable.

Surface area and porosity

The specific surface area (BET- N_2) values of the LDH samples are reported in Table 2. The LDH precursors $\text{Mg}_3\text{Al}-\text{CO}_3^{2-}$ and $\text{Mg}_4\text{Al}-\text{CO}_3^{2-}$ show a surface area in agreement with the values reported in the literature for similar samples prepared by the coprecipitation method and aging (in the range from 77 to 120 m^2/g) [31, 32]. Regarding CuPcTs intercalated samples, the surface area data indicated that no microporous products were produced in the intercalation. A substantial increase in the surface area values compared to the LDH precursors would be expected if microporosity was available. This assumption was confirmed by the N_2 adsorption-desorption isotherms of the intercalated LDHs. $\text{Mg}_3\text{Al}-(\text{CuPcTs})_{\text{int}}$ and $\text{Mg}_4\text{Al}-(\text{CuPcTs})_{\text{int}}$ exhibited type IV isotherms (not shown) characteristic of nonmicroporous materials with a hysteresis loop indicating interparticle mesoporosity, according to the IUPAC classification [33].

Despite the lack of microporosity it is noteworthy that the measured surface areas are higher than those reported by Carrado *et al.* [20]: 1.1 and 0.2 m^2/g for Mg–Al LDHs intercalated by CuPcTs through anionic exchange and coprecipitation method, respectively. Taking into account the surface area data, one can conclude that the synthetic strategy chosen to confine the guest species between the matrix layers has a considerable influence on the materials textural properties.

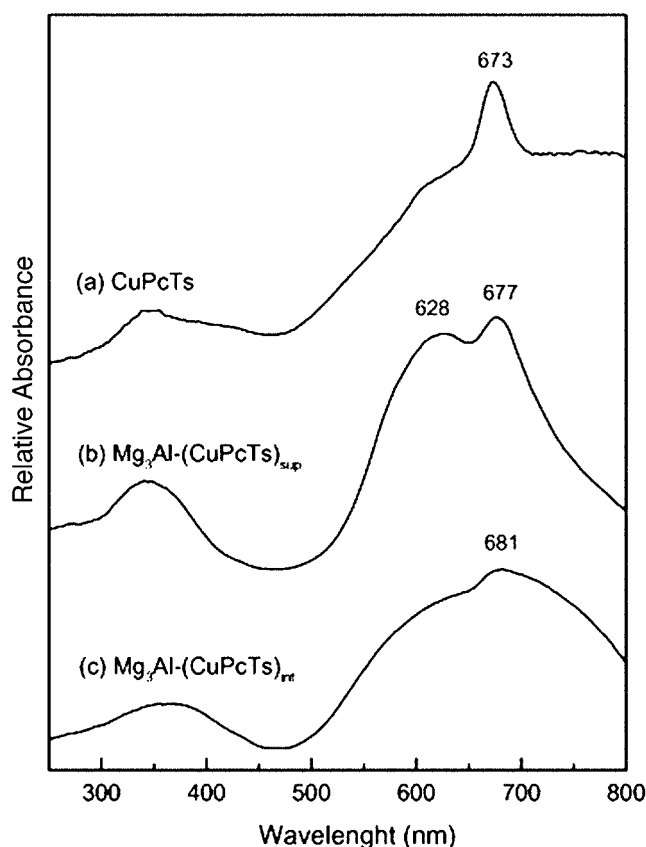


Figure 5. Diffuse reflectance spectra of (a) CuPcTs (sodium salt); (b) $\text{Mg}_3\text{Al}-(\text{CuPcTs})_{\text{sup}}$; and (c) $\text{Mg}_3\text{Al}-(\text{CuPcTs})_{\text{int}}$.

Electronic and vibrational spectra

Figure 5 shows the diffuse reflectance spectra of CuPcTs intercalated and supported on the Mg_3Al matrix (a similar spectral profile was obtained for the Mg_4Al system). For comparison purposes, the spectrum of CuPcTs in the solid state (sodium form) is also included in Figure 5.

The spectra show the two characteristic phthalocyanine absorption bands: the Soret or B band at about 350 nm and the Q band at ca. 670–680 nm (both are attributed to $\pi-\pi^*$ macrocycle ring transitions) [34]. In the solid state, the phthalocyanine electronic spectrum shows an overall broadening and a blue shift of the Q band as a consequence of dimerization and higher aggregates formation [34]. The strong absorption at 620–630 nm is related to the formation of dimeric species and a shoulder on the red side of the Q band is attributed to the aggregates. The CuPcTs spectral profile (Figure 5) reveals that the macrocycle is very aggregated in the solid state. The degree of phthalocyanine aggregation depends on the metallic cation and, in aqueous solution, it is observed that the dimerization constant for CuPcTs is high compared to other metallophthalocyanine tetrasulfonates [35]. For CuPcTs intercalated or supported on LDH, the aggregation degree decreases as noticed previously for the LDH-CoPcTs system [19]. In the intercalated sample, the guest molecule seems to be less dispersed than in the supported sample which is expected if we consider that the perpendicular arrangement between the LDH layers favors the macrocycle interaction conducting to dimer and

higher aggregates formation. In the supported sample, the macrocycle ring should be flat relative to the basal surface as suggested by our study about the interaction between CoPcTs and LDH [19].

The FT-IR spectra of the CuPcTs complex and the CuPcTs intercalated and supported on Mg_3Al were also recorded (not shown). The CuPcTs spectrum exhibited characteristic absorption bands at 602 and 638 cm^{-1} (benzene deformation), 698 cm^{-1} (macrocycle breathing), 746 and 835 cm^{-1} (macrocycle stretching), 924 cm^{-1} (benzene breathing), 1110 cm^{-1} (C–H bending), 1149 cm^{-1} (pyrrole breathing), 1332 cm^{-1} (C–C pyrrole stretching), 1400 cm^{-1} (isoindole stretching), 1504 cm^{-1} (C–N pyrrole stretching), 1030, 1192 and 1225 cm^{-1} (sulfonic groups) [36, 37].

The spectra of intercalated and supported LDH samples showed some bands attributed to the presence of CuPcTs in addition to a characteristic band attributed to the LDH framework (strong broad absorption band around 600 cm^{-1}) [31]. Comparing the CuPcTs complex spectrum and the CuPcTs intercalated and supported spectra, no significant band shifts were observed. On the other hand, some changes in the relative band intensities at 1330–1400 cm^{-1} were noticed. In this region, the changes were attributed to the carbonate ions present in the LDHs interlayer (ν_3 vibrational mode of CO_3^{2-}). This supposition was corroborated by elemental analysis data (Table I) that showed a slight carbon excess in the intercalated samples according to the C/N molar ratio. In relation to the supported samples, the presence of carbonate ions were expected because the CuPcTs molecules are located at the external surface and carbonate ions occupy the LDHs interlayer region.

EPR spectra

The obtained EPR spectrum in the solid state, at liquid nitrogen temperature, of the studied CuPcTs complex exhibited an isotropic value of $g = 2.051$, showing that the hyperfine splitting is too small to be resolved (spectrum not shown). Similar values were obtained with the CuPcTs supported compounds.

Also, the CuPcTs intercalation into LDHs did not seem to cause noticeable distortion of the coordination sphere of the metal. No hyperfine splitting due to the nuclear magnetic spin of the copper atom ($I = 3/2$), or nitrogen atoms ($I = 1$) in the macrocyclic ligand were detected (spectrum not shown). This behavior was similar to that observed for copper phthalocyanines encapsulated in zeolites which exhibited no significant differences in their EPR spectra in relation to the original complexes [38].

In contrast, the insertion of Schiff-base copper(II) complexes into β -cyclodextrin [39] caused an appreciable distortion of the coordination sphere of the metal, leading to an increase in the ligand field, in rhombic symmetry. Additionally, orientation dependent EPR signals were observed with CuTMPyP-hectorite (TMPyP is 5,10,15,20-tetrakis(1-methyl-4-pyridyl)-21*H*,23*H*-porphyrin), using oriented films of the intercalated complex [40]. Measurements were obtained with the silicate layers positioned perpendicular and parallel to the magnetic field. In both

cases, the framework around the complex had a substantial influence on its properties. However, in our case, using a similar experimental arrangement, the same isotropic signal was observed regardless of the orientation of the CuPcTs films on quartz flat cells with respect to the magnetic field. This result does not reject the possibility of a CuPcTs perpendicular orientation in the LDH gallery region as suggested by XRD data owing to the fact that we cannot assure unequivocally that the film was really oriented.

Hydrogen peroxide dismutation

Aiming at comparing the reactivity of the CuPcTs complex in solution and intercalated or supported on LDHs, manometric experiments of the catalyzed hydrogen peroxide decomposition were performed. Experimental curves of the released oxygen using the Mg₄Al system are shown in Figure 6. At pH 7.00 (non buffered solutions), the CuPcTs intercalated compound as well as the matrix Mg₄Al itself showed negligible catalytic activity, and the complex in solution showed very low activity (*ca.* 10%). When the reaction was performed at pH 7.99 (Figure 6a), the complex in solution exhibited a pronounced activity (190 μL O₂, after 90 min of reaction), corresponding to stoichiometric decomposition of the peroxide, after an induction period of 30 min. The LDH containing carbonate and the CuPcTs intercalated compound again showed negligible release of oxygen.

Similar results were obtained at pH = 9.59 (Figure 6b). In this case, both the CuPcTs–LDH samples showed very low activity (about 20%), while the CuPcTs complex in aqueous solution showed a rapid stoichiometric release of oxygen ($[O_2]/[H_2O_2] = 0.46$), with no detectable induction period (the LDH-carbonate does not show activity). It is well known that the hydrogen peroxide decomposition is favored in alkaline media [41].

These results indicated that only the free CuPcTs in solution is catalytically active, at pH ≥ 8.0 (the Mg₃Al systems showed a catalytic behavior similar to that reported to the Mg₄Al samples). The absence of reactivity is probably related to the central cation since we have noticed that some samples containing CoPcTs intercalated and supported on LDHs are active for H₂O₂ dismutation. According to the mechanism suggested in the literature [42] for the hydrogen peroxide dismutation by Cu(II) complexes, the lack of reactivity observed for the CuPcTs intercalated or supported samples can be due to (i) the hydroxide ion of the LDH structure is coordinated to the copper ion in an axial position, making difficult the OOH⁻ anion coordination at the sixth position (d⁹ configuration of Cu(II) is stabilized by Jahn–Teller effect); the CuPcTs species in the gallery region are aggregated which can hinder the access to the ion site, (ii) the CuPcTs interaction with the LDH layers is changing the redox potential of the Cu(I)/Cu(II) couple in a way that a higher potential is needed to reduce copper ion in the heterogeneous phase when compared to the homogeneous media. Despite the CuPcTs–LDHs compounds not showing catalase-like activity, the evaluation of these materials in catalyzed oxidative reactions with H₂O₂ (peroxidase-like reactions, hydroxylation) is not discarded. Kannan *et al.*

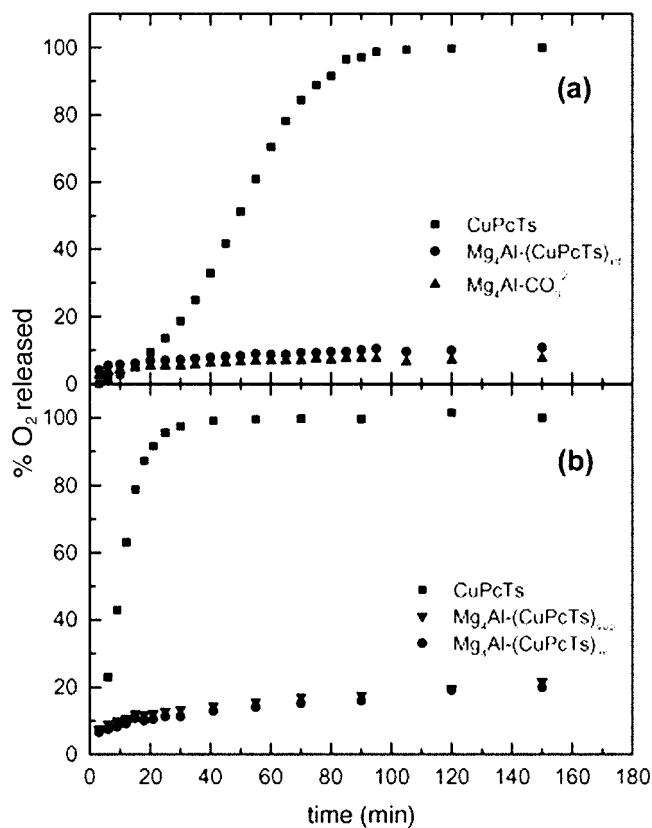


Figure 6. Oxygen released in the catalyzed dismutation of hydrogen peroxide (expressed in terms of % H₂O₂ decomposed) at (a) pH = 7.99 and (b) 9.59. Experimental conditions: (a) 2.7 mL of 6.2 mmol/L of H₂O₂; 0.30 mL of 25 mmol/L CuPcTs aqueous solution (corresponding to 6.3 μmol of Cu²⁺); 12 mg of Mg₄Al–CO₃²⁻ (30.1 μmol of Al³⁺); 21 mg of Mg₄Al–(CuPcTs)_{int} (8.3 μmol of Cu²⁺). (b) 2.7 mL of 5.4 mmol/L of H₂O₂; 0.30 mL of 25 mmol/L CuPcTs aqueous solution; 23.6 mg of Mg₄Al–(CuPcTs)_{int} (9.9 μmol of Cu²⁺); 70.0 mg of Mg₄Al–(CuPcTs)_{sup} (10.4 μmol of Cu²⁺).

[21] showed that cyclohexanol oxidation to cyclohexanone in acetonitrile is possible to occur in the presence of a CuPcTs–LDH compound employing hydrogen peroxide as the oxidant agent.

Conclusions

The CuPcTs complex was successfully intercalated in magnesium-aluminum LDHs by the reconstitution method as supported by characterization data. The extension of the metallophthalocyanine intercalated in LDHs was very high considering elementary analysis data. The IR vibrational spectra showed some weak bands that can be attributed to carbonate ions in the interlayer of the CuPcTs–LDH system. The CuPcTs immobilization between LDH layers was confirmed by the x-ray diffraction patterns: the basal spacing of the carbonate precursor (*ca.* 8 Å) increases to approximately 23 Å in the intercalated matrices.

The surface area and porosity analysis suggested that the materials containing CuPcTs intercalated in LDH do not have microporous structures. Although the Mg₄Al–(CuPcTs)_{int} material possesses less guest species between

the layers than the Mg₃Al analogous compound, microporosity was not achieved. Although the diffuse reflectance spectra revealed a decrease in the metallophthalocyanine aggregation in the intercalated or supported samples compared to the free complex, EPR spectra showed only the isotropic g value, evidencing that the CuPcTs aggregated species are dominant in the LDH samples. These data corroborated the surface area results, explaining the lack of microporosity for the intercalated compounds.

The CuPcTs intercalated LDHs show an appreciable thermal stability: decomposition begins to occur at ca. 400 °C and the DTG peak is observed at 447 °C. The localization of the CuPcTs species (intercalated or supported on LDHs) can lead to distinct decomposition products. The TGA technique is shown to be a useful tool to differentiate intercalated and supported materials, mainly for samples that show low crystallinity for XRD characterization.

LDH samples containing CuPcTs (intercalated or supported) show lower catalase-like activity than the free complex. The distinct catalytic performance may be due to modifications in the copper coordination sphere caused by immobilization.

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