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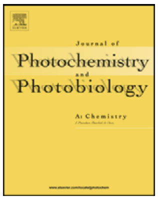

Laser flash photolysis of dioxo iron phthalocyanine intercalated in hydrotalcite and its use as a photocatalyst

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ABSTRACT

Dioxo iron phthalocyanine tetrasulphonate (FeO_2Pc) has been incorporated inside the intergallery space of a layered double oxide (LDH). Evidence for the inclusion of the FeO_2Pc inside the intergallery spaces of LDH was obtained from the expansion of the basal layer distance of the host. The resulting material (0.10–0.13 mmol $FeO_2Pc \times g^{-1}$) exhibits the optical spectrum characteristic of isolated metal phthalocyanine. Laser flash photolysis of the solid allows detecting the triplet excited state of the metal complex as a long-lived transient species whose decay is not complete in 2 ms. The solid is able to act as an effective photocatalyst for the degradation of aqueous phenol.

1. Introduction

Layered double metal hydroxides (LDHs) are lamellar materials constituted by sheets containing di- and trivalent metal cations in variable proportions octahedrally coordinated with hydroxide and oxy ligands [1]. The isomorphic substitution of di- by trivalent cations can be accomplished up to one fourth of the total positions and creates an excess of positive charge in the layer. This positive charge requires the presence of charge balancing anions that occupy the intergallery space of the solid [1–5].

LDHs have found wide application as basic solid catalysts [6–8]. One of the best studied LDH materials is Al/Mg LDH (Al/Mg ratio 0.33) containing carbonate as the charge compensating anion, and this material behaves as a solid base with a similar strength as some metal oxides and carbonates [6–9]. LDHs have also found application in the plastics industry as PVC additives employed to increase its thermal stability [10,11].

Besides these applications, LDH have also attracted interest as host materials that can intercalate organic anions or negative metallic complexes in the interlayer space [3,4,12]. The intergallery space can expand depending on the molecular size of the guest. Thus, in a certain way, LDHs are complementary materials to clays that are layered aluminosilicates that can host inside the layers positively charged species. Metal porphyrins have been incorporated inside the interlamellar spaces of clays and related aluminosilicate hosts such as zeolites [13–16]. The iron(III) porphyrin tetrasulphonate has been incorporated inside hydrotalcite and the resulting material used as oxidation catalyst [13]. It has also been reported that the incorporation of the iron porphyrin tetrasulphonate can be made during the synthesis of the layered material [14].

Layered clays have been used to develop photoresponsive solids in which the photochemical properties derive from the incorporated guest [16–18]. However, LDHs have received comparatively much less attention as materials to incorporate photoactive guests, and laser flash studies using LDHs as hosts have rarely been reported [16,18–29]. In the present work, we describe the preparation and characterization of the triplet excited state of an anionic dioxo iron phthalocyanine tetrasulphonate hosted within the interlamellar spaces of LDH (FeO_2Pc/LDH). FeO_2Pc has been previously found to be an excellent homogeneous catalyst for the hydrogen peroxide degradation of organic compounds [30,31]. Porphyrins are easily degradable by oxidation at the meso position and pyrrol rings. In contrast, metal phthalocyanines are structurally more robust and much less prone to undergo oxidative degradation, therefore they can exhibit high turnover numbers as oxidation catalysts [32–34]. Compared to the precedents in which porphyrins have been incorporated into LDHs [13–15,19,35,36], as far as we know, there are no reports on the incorporation of phthalocyanine into LDHs. Considering the photochemical response observed here, the resulting FeO_2Pc/LDH has potential applications in the development of photocatalysts and photoresponsive materials for solar light harvesting.

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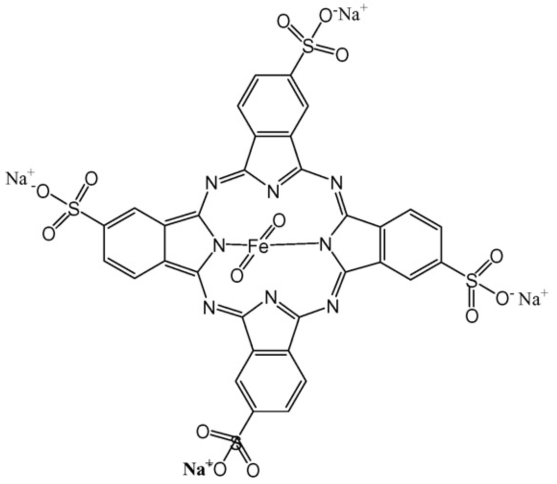

Chart 1. Chemical structure of the dioxo iron(IV) phthalocyanine (FeO_2Pc) used in this work.

2. Results and discussion

The LDH used in this work was obtained by precipitation using $CO_3{}^{2-}$ as base of a mixture of magnesium and aluminum nitrates as reported [13,14,37]. The Al/(Mg + Al) ratio was 0.25 and the charge compensating anion was carbonate. The solid was stirred with an aqueous solution of the mono sodium salt of the tetrasulphonic acid derivative of dioxo iron(IV) phthalocyanine (FeO_2Pc, Chart 1). Most metal Pc are extremely insoluble solids that tend to strongly aggregate either in concentrated solutions or in solid state. For this reason, we selected the tetrasulphonic derivate that is readily soluble in water; further, since it is an anion it can be readily introduced in LDH by ion exchanging a percentage of carbonate.

The success of the ion exchange was clearly evidenced by the diffuse reflectance optical spectrum of the FeO_2Pc/LDH that showed the presence of the highly colored complex. Fig. 1 shows a comparison of the transmission UV–vis spectrum of FeO_2Pc in aqueous solution compared to that of the FeO_2Pc/LDH recorded in the diffuse reflectance mode. The broader Q band recorded for the solid indicates that the iron complex aggregates when it is incorporated inside LDH at this loading.

The location of FeO_2Pc inside the intergallery spaces of LDH can be convincingly evidenced by observation of a shift in the (1 0 0) Bragg diffraction peak towards shorter angles indicating an expansion of the distance between the layers of the host material from 1.2 nm for the initial LDH to 1.7 nm in the host–guest complex. Fig. 2 shows the XRD patterns of the original hydrotalcite and the hydrotalcite containing FeO_2Pc. A control experiment submitting LDH to the same treatment in the absence of FeO_2Pc does not result in any change of the (1 0 0) diffraction peak. As it has been shown for related layered clays, intercalation of positively charged porphyrins and phthalocyanines causes a variation of the interlamellar space as a consequence of guest incorporation inside the gallery space [13–15,19]. In the case of iron(III) porphyrin tetrasulphone, it has been found that the metal complex is accommodated totally perpendicular to the LDH sheets [13]. The fact that the layer distance in FeO_2Pc/LDH is smaller than the dimensions of the guest can be rationalized assuming that the macrocycle is tilted inside LDH with respect to the perpendicular of the layers by an angle of 43°.

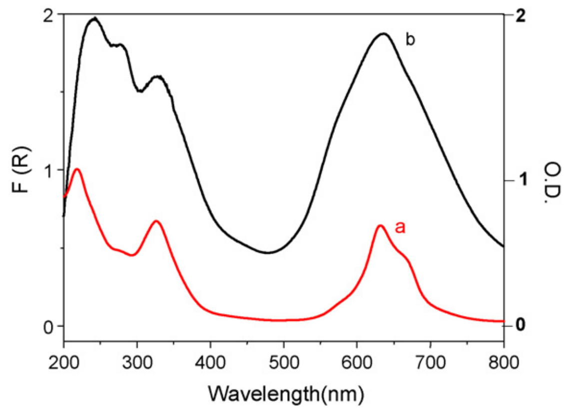

Fig. 1. Transmission UV–vis spectrum of an aqueous FeO_2Pc solution (a, O.D.) and diffuse reflectance UV–vis spectrum of FeO_2Pc/LDH (b, plotted as the Kubelka Munk function of the reflectance [38]).

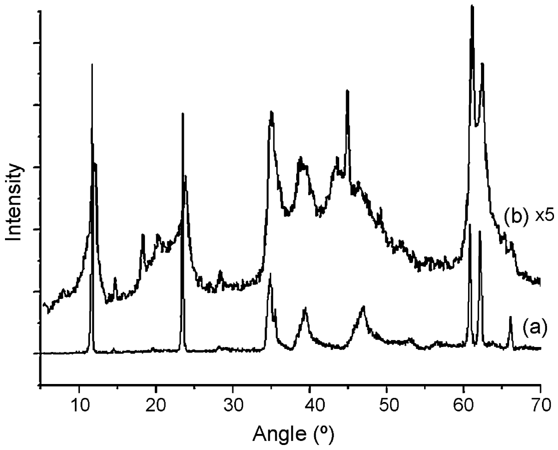

Fig. 2. Powder XRD of the original hydrotalcite (a) and after incorporation of FeO_2Pc (b). The diffractogram b has been shifted in the vertical axis and expanded five times for clarity.

The loading of FeO_2Pc was between 0.13 and 0.10 mmol as determined, respectively, by combustion elemental analysis of S (1.63%) and N (1.1%) that are present in the sulphonate group or in the macrocycle.

Diffuse reflectance laser flash photolysis of FeO_2Pc–LDH under nitrogen at 355 nm has allowed detecting a long-lived transient characterized by a broad absorption from 420 to 580 nm (Fig. 3). The transient is quenched by oxygen. Based on the similarity of the spectrum with that reported for the triplet excited state of metal phthalocyanines [39–41] and also on the oxygen quenching, we attribute this species to the electronic triplet excited state of FeO_2Pc.

The temporal profile did not exhibit noticeable differences in the wavelength range from 400 to 600 nm indicating that the spectrum

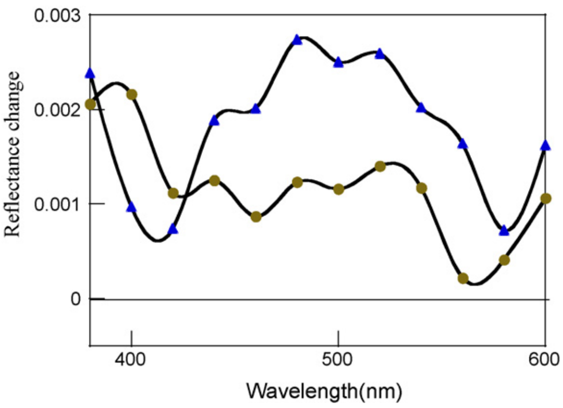

Fig. 3. Transient spectrum recorded at 100 μs (▲) and 1000 μs (●) after 355 nm excitation of N_2-purged FeO_2Pc/LDH sample.

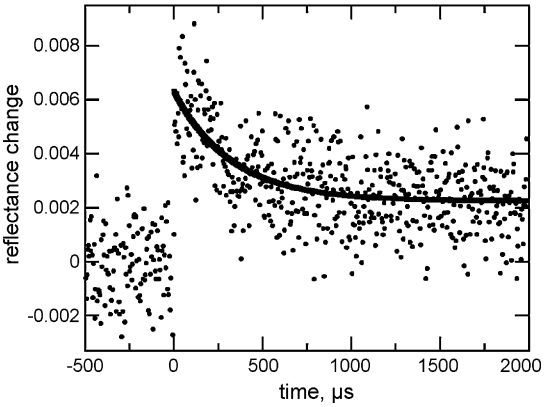

Fig. 4. Temporal profile monitored at 480 nm of the signal after 355 nm laser excitation of N_2-purged FeO_2Pc/LDH.

is due to a single transient species. This species is very long-lived and about two third of the signal do not decay in 2 ms after the laser pulse excitation, the longest time scale available in our nanosecond laser system (Fig. 4). Fitting of the signal decay (about one third of the total signal) to a first order kinetics as a first approximation gave a lifetime of 330 μs. It has been found that metal phthalocyanine in solution can act as a photocatalyst to cause the degradation of pollutants [42–46]. The most general photocatalytic mechanism involves the intermediacy of the triplet excited state of the metal complex and the generation of singlet oxygen [47]. The fact that LDH intercalated FeO_2Pc forms a very long-lived triplet excited state that is quenched by oxygen makes FeO_2Pc/LDH promising as a heterogeneous photocatalyst.

We wanted to test the photocatalytic activity of a solid material for the degradation of aromatic compounds. Phenol is one the favourite probe molecules to compare the photocatalytic activity of different materials [48]. In these assays the figure of merit is the percentage of phenol in neutral aqueous solution vs. time. Recently, we have determined that iron(III) phthalocyanines encapsulated inside zeolite Y cannot effect the degradation of phenol in aerated solutions without the assistance of hydrogen peroxide [49]. In the case of FeO_2Pc/LDH, Fig. 5 shows the time conversion plot for the photocatalytic degradation of phenol in the presence of FeO_2Pc/LDH. As it can be seen there, in contrast to the photocatalytic behaviour reported for Fe(III) phthalocyanines in zeolite NaY, FeO_2Pc/LDH is able to effect to a significant extent the degradation of phenol. The comparison between FeO_2Pc/LDH and FePc@NaY exemplifies the advantage of the material reported here.

In summary, LDH is a suitable host to include dioxo iron phthalocyanine inside its intergallery space. Expansion of the layer distance evidenced by powder XRD is a firm proof of the incorporation of FeO_2Pc in the intergallery space. Photochemical excitation gives rise to the formation of the triplet excited state as a very long-lived transient, capable of generating the reactive intermediates required for the catalytic degradation of aqueous phenol.

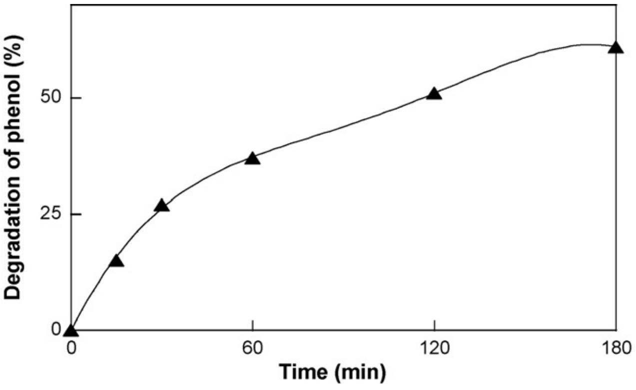

Fig. 5. Photocatalytic degradation of phenol (40 ppm) in aqueous solution (20 ml) in the presence of 30 mg of FeO_2Pc/LDH.

3. Experimental

3.1. Sample preparation

Hydrotalcite (LDH) was prepared by coprecipitation from an aqueous solution of magnesium and aluminium cations (solution A) and a highly basic carbonate solution (solution B). Solution A, containing $Mg(NO_3)_2\cdot 6H_2O$ and $Al(NO_3)_3\cdot 9H_2O$ dissolved in distilled water, was 1.5 M in (Al + Mg) with an Al/(Al + Mg) molar ratio equal to 0.33. Solution B was prepared by dissolving appropriate amounts of Na_2CO_3 and NaOH in distilled water in order to obtain $[CO_3{}^{2-}]$ equal to 1.0 M and a pH equal to 13 during the aging of the gel. In the synthesis procedure, solution B was placed in a 150 ml PTFE reactor and solution A was slowly dropped into it at a 60 ml/h rate under vigorous stirring at room temperature. The gel was stirred for more 140 min at room temperature and then aged under constant pH (13) for 18 h at 60 °C. The solid obtained was filtered and washed with hot distilled water until pH 7 and dried at 80 °C overnight.

FeO_2Pc as mono sodium salt was purchased from Aldrich and used as received. A suspension of LDH 5 g was magnetically stirred at 50 °C in 100 ml of a 10^{-2} M solution of the FeO_2Pc sodium salt in water at free pH for 3 h. After this time, the FeO_2Pc/LDH solid was collected, washed exhaustively with distilled water until the washings are colorless. Chemical analysis of the FeO_2Pc/LDH solid was carried out in a PerkinElmer CHNOS analyser that effects in a furnace the complete combustion of the organic material present in the solid. Diffuse reflectance UV–vis spectroscopy was performed in a Cary 5G using an integrating sphere and $BaSO_4$ as reference. Powder XRD patterns were recorded in a Philips X'Pert instrument using the Cu K_α radiation.

Laser flash photolysis measurements were performed using the third harmonic (355 nm) frequency of a Surelite Nd-YAG laser as the excitation source. Signals from the photomultiplier tube were captured and digitalized by a Tektronix 2012 transient digitizer and transferred to a computer using customized Luzchem software. Details of similar time-resolved diffuse reflectance systems have been described elsewhere [50]. Air-equilibrated FeO_2Pc/LDH samples were placed in a Suprasil quartz cuvette capped with a septum. The powder was flushed with N_2 or O_2 for at least 15 min before the experiments.

3.2. Photocatalytic test

Photocatalytic degradation of phenol was carried out by stirring at the open air at room temperature aqueous suspensions (20 ml) of phenol (40 ppm, pH 7) in the presence of the photocatalyst (30 mg). The suspensions were stirred for at least 10 min before irradiation. The samples were placed on a series of independent Pyrex test tubes (25 ml capacity) provided with magnetic stirring bar. The test tubes were placed in a thermostated water bath around a water-refrigerated Pyrex well containing a 125 W medium pressure Hg lamp. The course of the irradiation was followed by taking one test tube at the required reaction time and analysing the supernatant aqueous solution as well as the material retained in the solid. The solids were extracted by sonicating the powder redispersed in 3 ml of fresh water. The combined extracts (supernatant plus products recovered from the solid) were analysed by reverse phase HPLC (suprasil column, diode array detector monitoring at 254 nm). Blank controls stirring a suspension of FeO_2Pc/LDH and phenol in the dark showed that our extraction procedure is able to recover over 85% of the initial mass.

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