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Immobilization of metallophthalocyanines on hybrid materials and in-situ synthesis of pseudo-tubular structures from an aminofunctionalized kaolinite

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ABSTRACT

The results from a study of the immobilization of cobalt(II) tetracarboxyphthalocyanine on a kaolinite functionalized with tris(hydroxymethyl)aminomethane are presented. The resulting materials were characterized by X-ray diffraction, thermal analyses, infrared and ultraviolet–visible absorption spectroscopy, and scanning and transmission electron microscopy. The detection of some bands typical of cobalt(II) tetracarboxyphthalocyanine by infrared spectroscopy confirmed immobilization of the complex on the amino-functionalized kaolinite and showed that there were no alterations in the interlayer hydroxyl groups of kaolinite, and also evidenced that immobilization occurred via the amine. The X-ray diffraction analysis revealed that the immobilization process prompted a structural change in the functionalized kaolinite, leading to the formation of a non-layered material. Solid state UV–Vis spectroscopy attested to the immobilization of the cobalt(II) tetracarboxyphthalocyanine on the amino-functionalized kaolinite, as verified from the appearance/displacement of some bands characteristic of the metal complex.

1. Introduction

Metallophthalocyanines (MPcs) belong to a class of synthetic compounds that closely resemble natural porphyrins, with the advantage that they are much more chemically and physically stable [1,2].

Some authors [3,4] mention that one disadvantage of MPcs is their poor solubility in an aqueous media and in a number of organic solvents, which limits their use in homogeneous catalysis. This drawback can be overcome by substituting the peripheral groups of MPcs with sulfate or carboxylate, as in the case of cobalt(II) tetracarboxyphthalocyanine (II) (Co(II)MPc, Fig. 1).

However, De Oliveira et al. [5] have reported on the difficult separation of water-soluble MPcs, which restricts their application as photocatalysts and makes their incorporation into inorganic matrices necessary. These authors presented results for phthalocyanine attached to mesoporous silica, which found potential application in pesticide photodegradation. Indeed, excellent catalytic activity was achieved for the immobilized phthalocyanine, with yields increasing from 40 to 90% ongoing from homogeneous to heterogeneous media [5]. Ernst et al. have also published data on the catalytic activity of MPcs immobilized onto molecular sieves, which gave much better yields as compared to the free compound in homogeneous solution [6]. Apart from the aforementioned works there are countless articles describing the advantages of employing MPcs immobilized on various matrices for heterogeneous catalysis. Such advantages include facile separation from the product from the catalyst, recycling, and reuse of these catalysts, not to mention their higher catalytic activity [7,8].

MPc immobilization on an inorganic matrices allows for better dispersion of the macromolecules. This enables better exploration of the MPc properties, since in aqueous medium (and in some other solvents) these complexes form aggregates. Moreover, immobilization provides enhanced stability as well as improved thermal and chemical resistance [5,6]. In this context, layered clay minerals have been widely employed as supports for the immobilization of compounds for a variety of applications [9,10]. Among the clay

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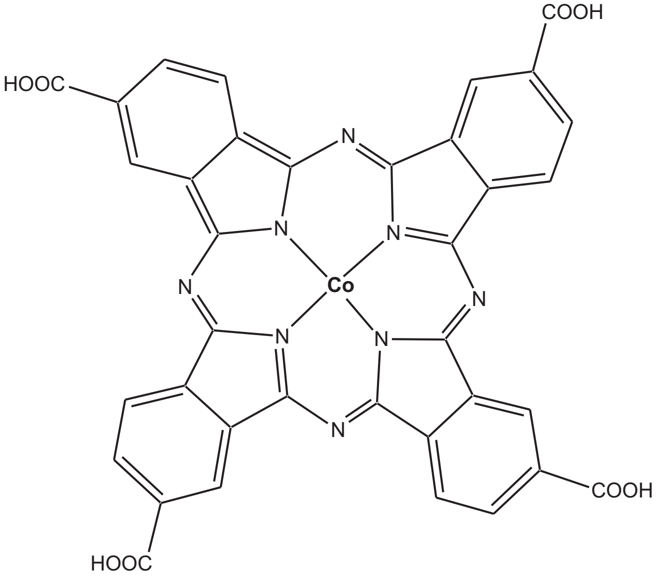

Fig. 1. Molecular structure of cobalt(II) tetracarboxyphthalocyanine (Co(II)MPc).

minerals, kaolinite stands out as an inorganic support for the immobilization of some interesting compounds, such as metalloporphyrins and other complexes [11–13].

Kaolinite is a clay mineral of the 1:1 layer type, with theoretical formula $Al_2Si_2O_5(OH)_4$ and basal spacing of 7.20 Å. Clay minerals of the 1:1 type (or TO) are formed by combination of tetrahedral SiO_4 sheets (T) and octahedral $Al(OH)_6$ sheets (O) at a 1:1 ratio [14,15]. Because these layers interact via hydrogen bonding, the intercalation process in this space requires previous intercalation with highly polar molecules such as dimethylsulfoxide (DMSO) or *N,N*-di-methylformamide (DMF) [16–18], in order to allow for clay interaction with larger molecules and its further functionalization.

Kaolinite functionalization with a series of organic species has already been studied. The attainment of hybrid materials with pyridine-carboxylic acids and amine [19,20], alcohols and amino alcohols [18,21,22], and porphyrins [12] has been reported.

Motivated by the potential application of MPcs and the properties of functionalized kaolinite, this work studied the immobilization of Co(II)MPc onto kaolinite functionalized with tris(hydroxymethyl) aminomethane (Ka-TRIS). The prepared materials were characterized by X-ray diffraction (XRD), thermal analyses (TG/DTG), infrared (IR) and ultraviolet–visible (UV–Vis) absorption spectroscopies, and scanning (SEM) and transmission (TEM) electron microscopies.

2. Experimental

2.1. Kaolinite purification

The clay mineral employed in this work was supplied by Mineradora Darci R. O. Silva Ltda., situated in the municipality of São Simão, state of São Paulo, Brazil. The clay was purified, for impurities removal. The clay was purified by the dispersion settling method [19,23], and the purified kaolinite was designated Ka.

2.2. Intercalation with DMSO

The methodology employed for the preparation of the kaolinite precursor intercalated with DMSO (Ka-DMSO) was based on a process previously described by our group [10,19], which consists in a modification to the process reported by Detellier et al. [24]. To this end, Ka (40 g) was suspended in DMSO and distilled water (1 g Ka/6.75 mL DMSO/0.75 mL distilled water) for 10 days under magnetic stirring, at 60 °C.

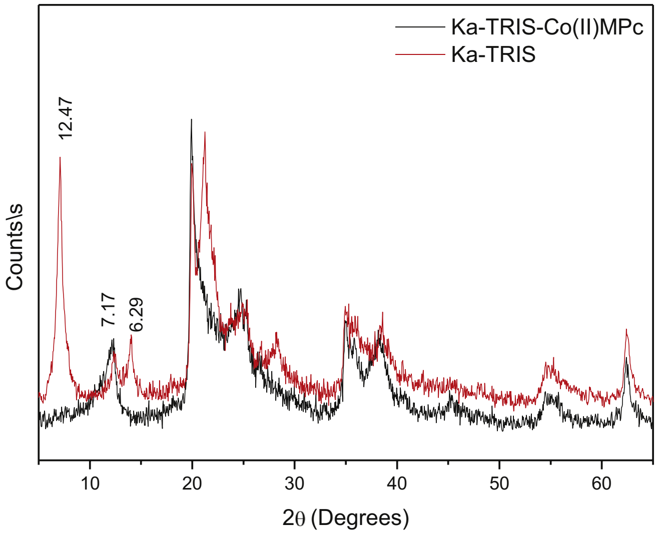

Fig. 2. X-ray diffractogram of the materials Ka-TRIS and Ka-TRIS-Co(II)MPc.

2.3. Preparation of the Ka-TRIS hybrid material

The hybrid material Ka-TRIS was prepared by means of a previously published methodology [22,25]. Briefly, TRIS (24 g) was heated in the presence of the intercalated material Ka-DMSO (10 g) at a Ka-DMSO/TRIS molar ratio of 1:5, until TRIS had completely melted. This procedure was accomplished under reflux at 180 °C, for 48 h.

2.4. Cobalt(II) tetracarboxyphthalocyanine immobilization on amine-functionalized kaolinite

Co(II)MPc was synthesized, purified, and characterized according to Csokai [26], and it was then incorporated into the hybrid material Ka-TRIS at a 1:10 Ka-TRIS/Co(II)MPc molar ratio. First, Co(II)MPc was suspended in distilled water and kept under constant stirring for solubilization. In the presence of the hybrid material, Co(II)MPc generated a blue suspension, which was maintained under magnetic stirring for 10 min. The resulting material was washed with distilled water and dried in an oven at 100 °C, affording the hybrid designated Ka-TRIS-Co(II)MPc.

2.5. Grafting test – resistance to hydrolysis

Resistance to hydrolysis, usually designated functionalization test, was investigated for Ka-TRIS-Co(II)MPc. Then 50 mg of kaolinite containing the Co(II)MPc was magnetically stirred in 10 mL of distilled water for seven days. After this period the solid

Table 1
Attribution of the Miller indices for Ka-TRIS-Co(II)MPc.

2*θ* (degrees)	Miller indices (hkl)
12.33	001
19.92	100
24.76	002
35.04	110
38.36	003
55.76	210
62.40	300