

Article II

New strategies for synthesis and immobilization of methalophtalocyanines onto kaolinite: Preparation, characterization and chemical stability evaluation.

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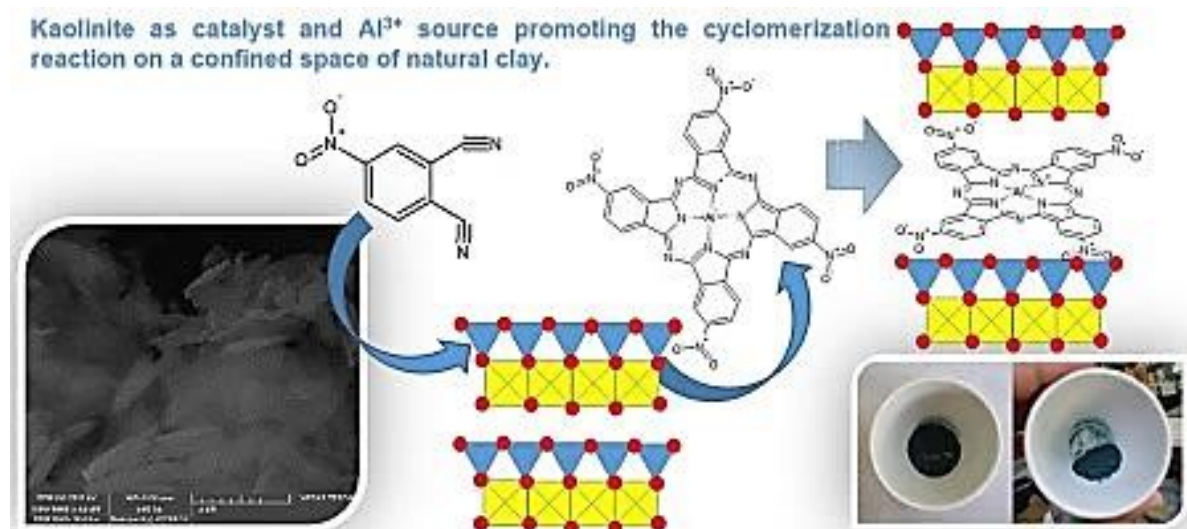
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ABSTRACT

This study presents results concerning the one-step synthesis and immobilization of a metallophthalocyanine on kaolinite as support/catalyst. X-ray diffractometry (PXRD), nuclear magnetic resonance (NMR) and infrared (FTIR), UV/Visible (UV/Vis) and X-ray photoelectron (XPS) spectroscopies, thermal analyses and scanning electron microscopy (SEM) aided for the characterization of the materials. The FTIR, XPS and UV/Vis absorption spectra confirmed metallophthalocyanine formation. XRD analysis provided data on the structural disorganization of kaolinite during the synthesis of metallophthalocyanine, corroborated by SEM. NMR revealed that partial dissolution of aluminum from the octahedral kaolinite sheets was possible, which should release Al into the medium and, together with phthalonitrile, promote cyclomerization of the phthalocyanine macrocycle.

Keywords: Phtalocyanines, Immobilization, Hybrid materials, Clays, Nanocomposite

Introduction

Phthalocyanines are symmetric aromatic macrocycles consisting of benzopyrrole rings connected by nitrogen bonds (Kaya et al., 2010; Zawadzka et al., 2014). This arrangement gives rise to a π electron conjugation that provides phthalocyanines with high absorption coefficient in the UV/Visible region, stable electron configuration, and excellent optical properties (Kadish et al., 1999; Kimura et al., 2003).

The first methods developed for the synthesis of metallophthalocyanines involved slow reactions that required high temperatures. In most cases, these conditions culminated in relatively low yields because the reactants underwent degradation and subproducts emerged in the reaction medium (Nyokong and Ahsen, 2012). Over the last decades, new techniques have been developed to increase process yield and make the synthesis of metallophthalocyanines more selective. For example, cyclotetramerization of precursors derived from phthalonitriles, phthalimides, phthalic anhydride, and others has enabled the synthesis of metallophthalocyanines in moderate yields (Lukyanets and Nemykin, 2010; Mack and Kobayashi, 2011).

In aqueous medium, metallophthalocyanines form aggregates that make dispersion difficult. Metallophthalocyanine immobilization on inorganic matrixes minimizes this issue, reaching the atomic molecular scale. Moreover, immobilization increases thermal and chemical stability, improving the properties of metallophthalocyanines (De Oliveira et al., 2008; Ernst and Selle, 1999).

The synthetic routes available to prepare metallophthalocyanines demand significantly long purification steps and excessive amounts of energy. These routes also require the use of a variety of solvents and metallic salts or metals for phthalocyanine cyclomerization, which can contaminate the environment. To meet the principles of green chemistry and sustainability when synthesizing metallophthalocyanines, researchers have searched for new routes that demand less energy and little or no metal or metallic salt as the starting reactant. Other research activities aimed to improve the properties of metallophthalocyanines by immobilizing them on inorganic matrixes (Da Silva et al., 2014).

The use of inorganic matrixes as a source of metallic ions for metallophthalocyanine cyclomerization has become an interesting alternative—matrixes can donate metal ions and

act as support/catalyst for the synthesized metallophthalocyanines, promoting immobilization and enhancing the physicochemical properties of these macromolecules.

Clay minerals have been commonly employed as support to immobilize many substances (Avila et al., 2010; Bhattacharyya and Gupta, 2008; Yang et al., 2012). In this context, kaolinite has stood out for its natural abundance, physicochemical properties, and lamellar structure. Kaolinite constitutes an important industrial raw material for immobilization of metallophthalocyanines (Da Silva et al., 2014), porphyrins (Bizaia et al., 2009; Machado et al., 2012), and other complexes (De Faria et al., 2011), to generate hybrid organic-inorganic materials with interesting properties.

Motivated by the possibility of obtaining metallophthalocyanines by new synthetic routes, in this work we present the preparation and immobilization of metallophthalocyanine on kaolinite in a single step, aiming to save energy, reduce solvent consumption, and comply with the principles of green chemistry and sustainability.

Driven by the ability to synthesize metallophthalocyanines by new synthetic routes, this work shows the study of the aluminum metallophthalocyanines synthesis using kaolinite as aluminium source and support, the immobilization of the synthesized complex in a single step are discussed, aiming energy saving, solvent and while reaching the precepts of green and sustainable chemistry, wherein the aluminium was generated in situ during the synthesis.

The solids could be applied as heterogeneous catalysts, and in photodynamic therapy, photooxidation reactions and photodegradation of pollutants. The great problem in use conventional metallophthalocyanines is the agglomeration of these complexes. However using the complexes immobilized into layered kaolinite we prevent the aggregation in the axial position and also increase the activity.

Experimental

The procedures used to purify the clay mineral and to intercalate dimethylsulfoxide (DMSO) into its interlayer space were carried out as described in other literature articles authored by members of our research team (Da Silva et al., 2014; de Faria et al., 2010).

Synthesis and immobilization of metallophthalocyanine on kaolinite

Phthalonitriles, which are precursors of phthalocyanines, bear groups that can interact with groups in the kaolinite structure. This allows immobilization of the precursor on the matrix, followed by metallophthalocyanine formation. One-step synthesis and immobilization of metallophthalocyanines on kaolinite required the use of kaolinite intercalated with DMSO (KaDMSO) and 4-nitrophthalonitrile (PCNO₂) at a 3:1 KaDMSO/PCNO₂ (m/m) ratio. This mixture was kept at 150 °C for 48 h. After washing with acetone and separation by centrifugation, the resulting material (designated KaPCNO₂) was characterized. Data were compared with the results obtained for aluminum (III) tetranitrometallophthalocyanine (Al(III)TNMPC) obtained by conventional route using solvent and conventional aluminium source from metallic salt according Shaposhnikov (Shaposhnikov et al., 2005), that consisting in react one organic ligand that containing nitro groups (4-nitrophthalonitrile) in contact with metallic specie at temperature near to 210-220 °C. Fig. III.1 shows a schematic representation of the new synthetic route used to prepare and immobilize metallophthalocyanine on kaolinite.

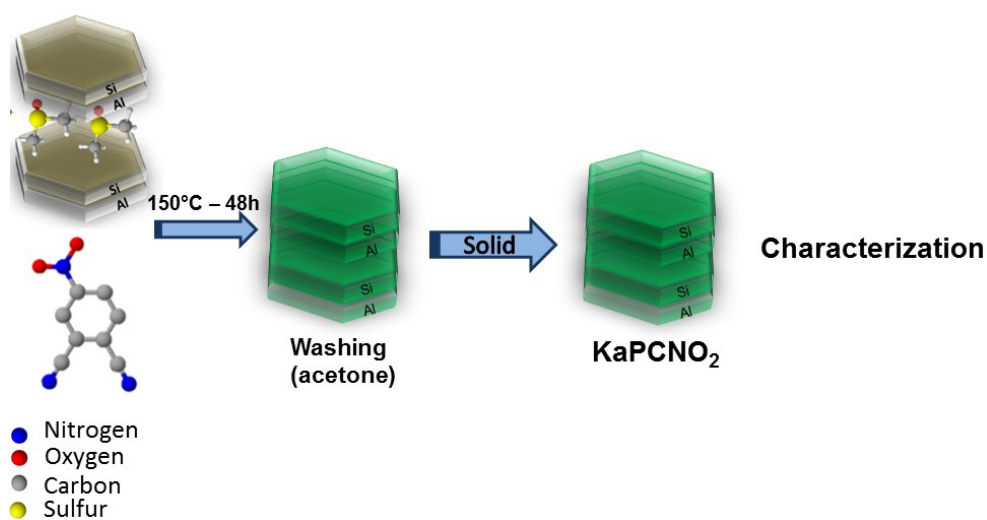


Figure III.1: Schematic representation of the new synthetic route used to prepare and immobilize metallophthalocyanine on kaolinite.

Characterization techniques

The powder X-ray diffractograms (PXRD) of the solids were recorded on a Miniflex II–RIGAKU diffractometer operating at 30 kV and 15 mA (1200 W), using filtered Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). The angle 2θ varied from 2 to 65°. All the analyses were undertaken at a scan rate of 2° (2θ) per minute.

Thermal analyses were performed on a TA Instruments–SDT Q600–Simultaneous DTA-TGA analyzer. The samples were heated from 25 to 900 °C at a heating rate of 20 °C per minute, in oxidizing (air) atmosphere, at a flow rate of 100 mL/min.

Infrared (FTIR) absorption spectra were acquired on a Perkin Elmer FT-IR Frontier Spectrometer by using a diffuse reflectance accessory. Detailing, 1 mg of each solid were mixed with 100 mg of KBr and finely pulverized until the complete dilution of each solid in KBr. Solids rich in organic ligands (e.g. aluminium metallophthalocyanine were diluted 0.1 mg with 100 mg of KBr. The powder obtained in a typical holder and finally the samples inserted in the FTIR equipment and analyzed. The number of scans acquisitions were 32 per spectrum the resolution of 1 cm^{-1} was employed.

For the ultraviolet/visible (UV/Vis) absorption spectra, the samples were placed in cells with 10-mm optical path length. The spectra of liquid and solid samples were recorded on a DiodeArray UV-Vis spectrophotometer HP mod. 8453 and on a OceanOptics Fluorimeter, respectively.

The X-ray photoelectron spectroscopy (XPS) was carried out at a pressure of less than 10^{-7} Pa using a commercial spectrometer (UNI-SPECS UHV). The Mg K α line was used ($h\nu = 1253.6 \text{ eV}$) and the analyzer pass energy was set to 10 eV. The inelastic background of the Al 2p, Si 2p, N 1s, O 1s and C 1s electron core-level spectra was subtracted using Shirley's method. The binding energy scale of the spectra was corrected using the C 1s hydrocarbon component of the fixed value of 285.0 eV. The spectra were fitted without placing constraints using multiple Voigt profiles.

Nuclear magnetic resonance spectra were registered on a Bruker apparatus model AVANCE III, 9.4 Tesla (400 MHz for hydrogen frequency), equipped with a 4-mm CP/MAS probe for solid samples and a 10-mm BBO probe for liquid samples.

Scanning electron microscopy images were obtained on a TESCAN VEJA 3 SBH apparatus equipped with 30-kV W filament, (3-nm resolution), and SE and BSE detectors.

The textural analyses were accomplished from the corresponding nitrogen adsorption/desorption isotherms at -196°C, obtained in a static volumetric apparatus

(Micromeritics Model ASAP 2020 adsorption analyzer). The samples (0.2 g) were degassed at 150°C for 24 h. The specific surface area (S_{BET}) was obtained by the BET method, and the total pore volume was calculated from the amount of nitrogen adsorbed at a relative pressure of 0.95.

Results and discussion

Characterization of Ka and KaDMSO provided results that agreed with literature data and confirmed the lamellar nature of kaolinite and DMSO intercalation into the clay (Da Silva et al., 2014; de Faria et al., 2010).

UV/Vis absorption spectroscopy

Fig. III.2 shows the UV/Vis spectra of KaPCNO₂ and Al(III)TNMPC. These spectra confirmed formation of the metallophthalocyanine.

Both spectra displayed the typical bands of metallophthalocyanines: the Soret band between 300 and 350 nm and the Q band between 600 and 700 nm (Kadish et al., 1999; Kimura et al., 2003). More specifically, these bands were located at 338 and 695 nm in the spectrum of Al(III)TNMPC, respectively, and at 341 and 620 nm in the spectrum of KaPCNO₂, respectively. Comparison of the two spectra and the band shifts evidenced formation of the metallophthalocyanine and its immobilization on the functionalized kaolinite.

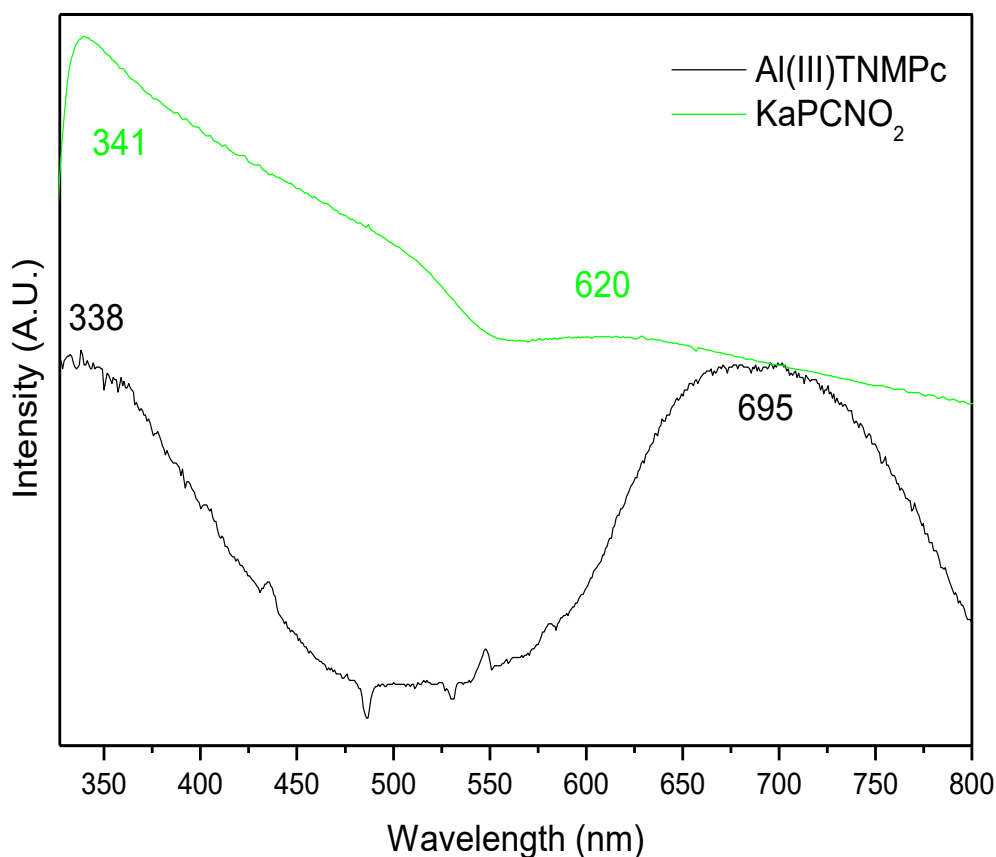


Figure III.2: UV/Vis spectra of Al(III)TNMPC and KaPCNO₂.

FTIR spectroscopy

Fig. III.3 and Table III.1 display the FTIR spectra and the major band assignments for Al(III)TNMPC, Ka, KaPCNO₂, and PCNO₂, respectively.

The FTIR spectra also attested to metallophthalocyanine formation. Bands due to C=N group vibration emerged at 1616 and 1611 cm⁻¹ for KaPCNO₂ and Al(III)TNMPC, respectively, while the spectrum of the precursor PCNO₂ did not contain this band. The vibrations related to the NO₂ group appeared at 1337, 1405, 1520, and 3094 cm⁻¹ in the spectrum of Al(III)TNMPC, and at 1344, 1421, 1527, and 3097 cm⁻¹ in the spectrum of KaPCNO₂. As for PCNO₂, the bands due to N=O group vibration arose at 1356, 1411, and 1538 and between 3085 and 3116 cm⁻¹ (Bahadoran and Dialameh, 2005; Karaođlan et al., 2011; Shaposhnikov et al., 2005; Zhou et al., 2009). The changes observed and displacements in the FTIR spectra of the solids compared to kaolinite confirm the interaction of NO₂ groups from Al(III)TNMPC synthesized in situ with kaolinite interlayer hydroxyl groups.

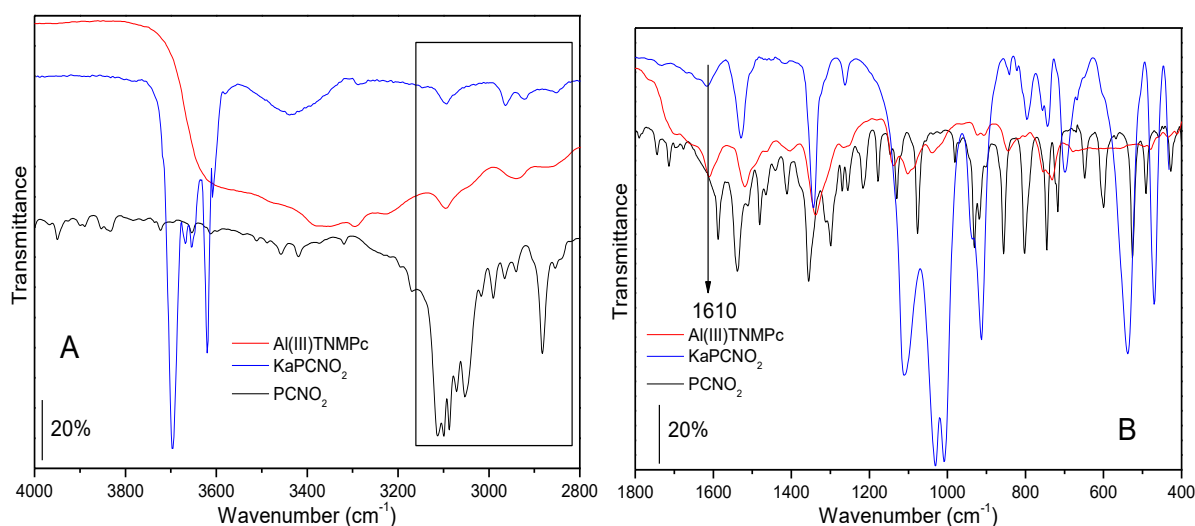


Figure III.3: FTIR absorption spectra of Al(III)TNMPC, Ka, KaPCNO₂, and PCNO₂ separated by regions: A – from 4000 cm⁻¹ to 2800 cm⁻¹; B – from 1800 cm⁻¹ to 400cm⁻¹.

Table III.1: Assignment of the main FTIR absorption bands

	Ka (cm ⁻¹)	Al(III)TNMPC (cm ⁻¹)	PCNO ₂ (cm ⁻¹)	KaPCNO ₂ (cm ⁻¹)
νOH	3696	-	-	3697
inter νOH	3668, 3654,	-	-	3668, 3654, 3620
intra νN=O	-	1337, 1405, 1520, 3094	1356, 1411, 1538, 3085-3116	1344, 1421, 1527, 3097
νC=N	-	1611	-	1616

XPS analysis

Additional evidence for the formation of aluminum(III) phthalocyanine was obtained by the analysis of XPS N 1s and Al 2p core-level spectra. Fig. III.4a displays the N 1s spectra obtained for the PCNO₂ precursor and the KaPCNO₂ product. For PCNO₂ the component related to nitric oxide, located at 405.5 eV, is separated from the nitrile group (399.2 eV) by about 6.3 eV (Naumkin et al., 2012). The formation of pyrrole-like bonds (C=N-C) induces a shift of the low binding energy component to 398.7 eV (Naumkin et al., 2012). Another indication for the extraction of Al(III) from kaolinite under formation of aluminum(III) phthalocyanine comes from the Al 2p spectra, when comparing kaolinite with KaPCNO₂. The spectrum of Ka can be fitted with a single component at 75.3 eV, related to Al of the octahedral sheets bonded to Si occupying the tetrahedral layer (Naumkin et al., 2012). The low energy component (74.2 eV), detected in the spectrum of KaPCNO₂, is indicative for Al(III) species in metallophthalocyanine. Taking in account the low sampling depth of XPS of about 5 nm, the noisy Al 2p spectrum of KaPCNO₂ results from attenuation effect of kaolinite caused by the wrapping effect of phtalocyanine macromolecules. Furthermore, the quantitative analysis confirmed the nominal composition of TNMPC (61.5 at.% C, 23.1 at.% N, 15.4 at.% O), within an error of ±10%. No signal of sulfur was detected in the spectra, indicating the absence of residual DMSO.

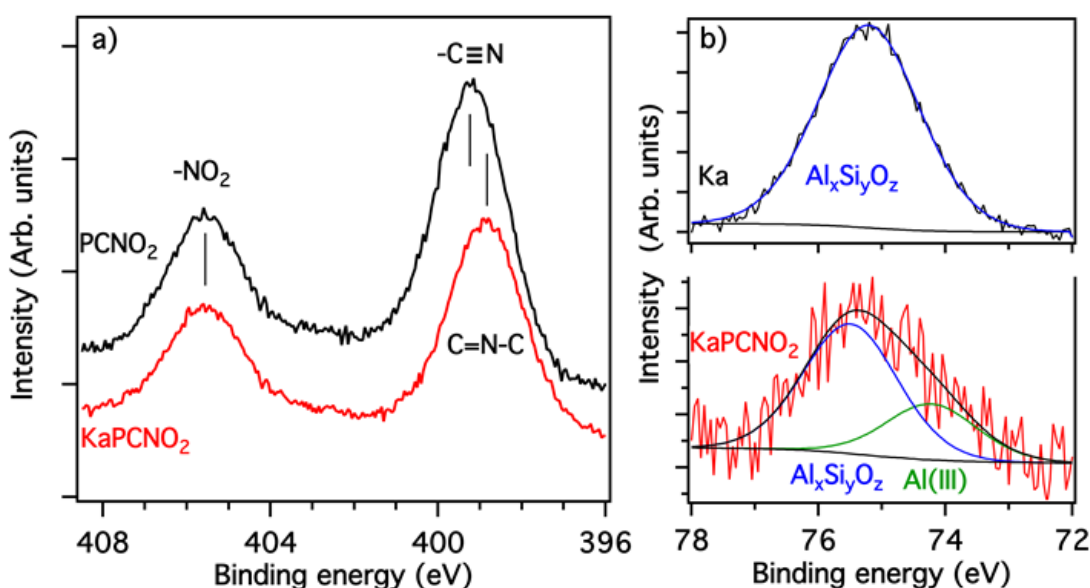


Figure III.4: XPS a) N 1s spectra of PCNO₂ and KaPCNO₂, b) fitted Al 2p spectra of Ka and KaPCNO₂

PXRD analysis

Fig. III.5 depicts the diffractograms recorded for Ka and KaPCNO₂. The XRD patterns evidenced the structural modifications that the metallophthalocyanine synthesis promoted in kaolinite.

The diffractograms of KaDMSO and KaPCNO₂ were different. Structural modifications experienced by kaolinite during metallophthalocyanine synthesis were evident in the diffractogram of KaPCNO₂. Crystalline order decreased during the synthesis—the peaks due to reflections d₀₂₀ and d₀₀₂ broadened, and the peak relative to reflection d₁₁₁ disappeared. Therefore, metallophthalocyanine synthesis made kaolinite more disorganized due to clay exfoliation/delamination and/or partial dissolution (Araújo et al., 2014; Da Silva et al., 2014; Nakagaki et al., 2006; Valášková et al., 2007). The low-intensity peak at 2θ = 6.12°, corresponding to a basal spacing of 14.42 Å, was compatible with metallophthalocyanine intercalated into kaolinite interlayer space, obviously this space is not compatible with perpendicular orientation of Al(III)TNMPC, probably this large complex presents parallel orientation in relation to interlayer space of clay. The same effect was previously observed in the previous work using metalloporphyrins into grafted clay (Bizaia et al., 2009). Another point that could be emphasized is that treatment removes completely the DMSO molecules from interlayer space of kaolinite and results in the small effect at 14.42 Å assigned to 4-nitrophthalonitrile intercalated and also the parallel orientated Al(III)TNMPC into kaolinite interlayer spaces.

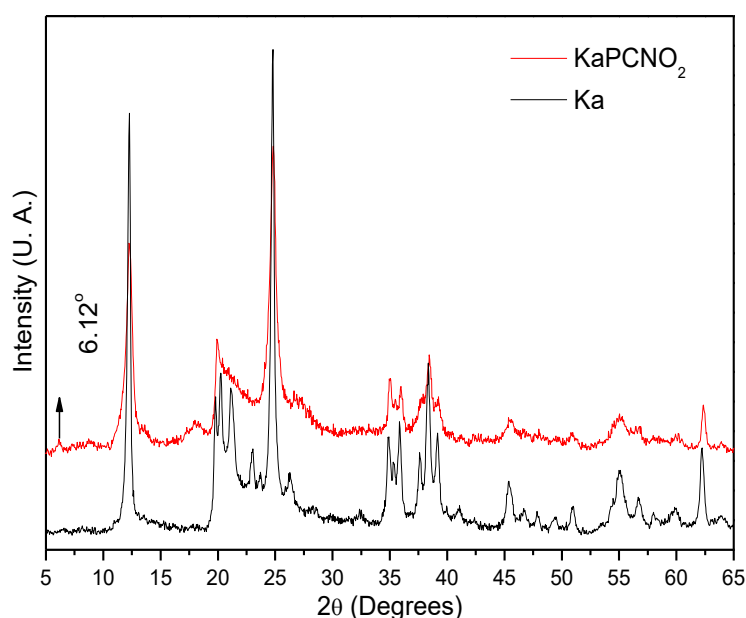


Figure III.5: Diffractograms of Ka and KaPCNO₂.

Thermal analyses

Fig. III.6 presents the TG/DTG curves obtained for Ka, KaPCNO₂ and Al(III)TNMPC. Comparison of the thermal analyses of Ka and KaPCNO₂ revealed that have similar profiles, with small differences due to the presence of the metallophthalocyanine (Al(III)TNMPC).

The TG/DTG curves of Al(III)TNMPC showed a mass loss below 100 °C, due to moisture water, as well as mass losses relative to metallophthalocyanine degradation at maximum temperatures of 474 and 509 °C. Comparison of the TG/DTG profiles of KaPCNO₂ and Al(III)TNMPC showed that the thermal events occurred at similar temperatures. Because the metallophthalocyanine degradation temperatures were close to the temperature at which kaolinite dehydroxylation took place, the mass losses at 464, 514, and 555 °C could result from both metallophthalocyanine degradation and the dehydroxylation process. However, analysis of the TG/DTG curves of KaPCNO₂ showed that this material contained organic matter—the percent mass loss of purified Ka and KaPCNO₂ was 15 and 24%, respectively, and the higher mass loss in the case of KaPCNO₂ could be due to the presence of the metallophthalocyanine synthesized in situ on kaolinite.

Based on this mass loss and as demonstrated in the literature (Silva et al., 2012), it was possible to calculate the amount of synthesized metallophthalocyanine—1.05 mol of metallophthalocyanine per mol of kaolinite.

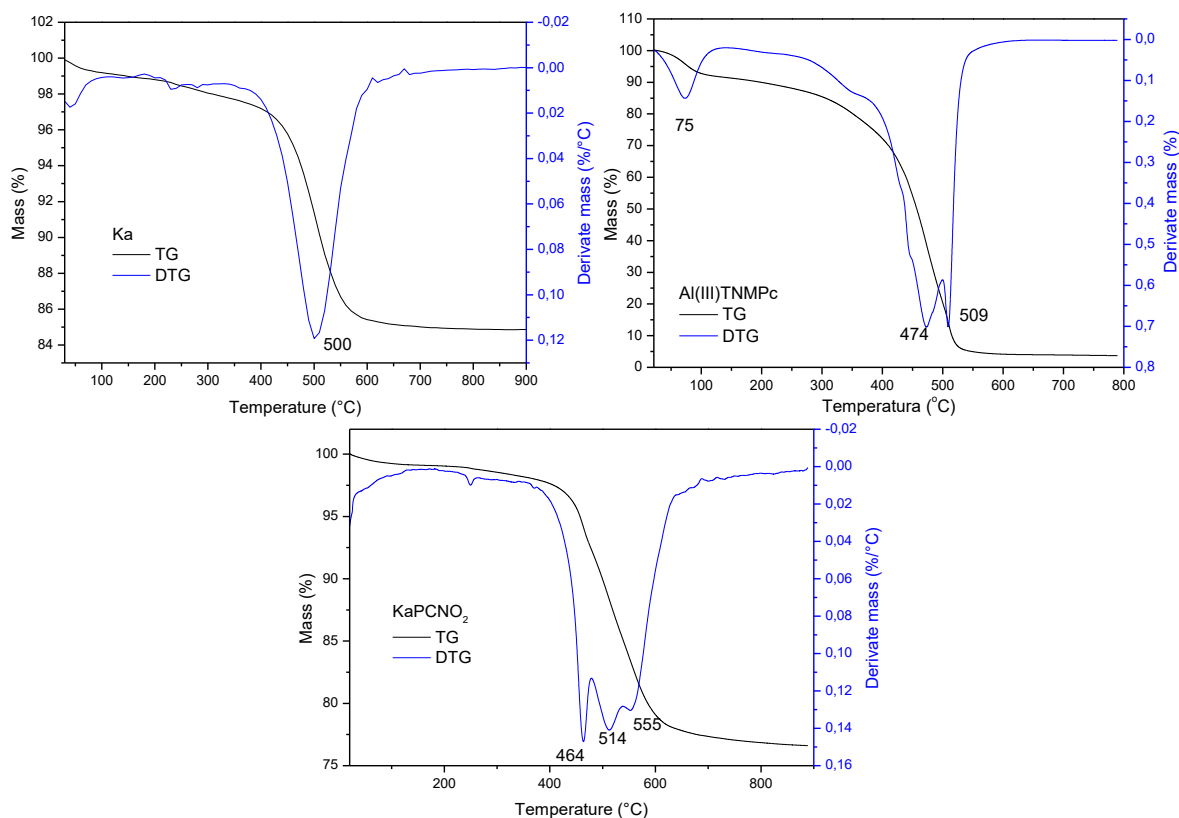


Figure III.6: TG/DTG curves obtained for Ka, Al(III)TNMPC, and KaPCNO₂.

The DTA curves (Fig. III.7) obtained for Ka showed an endothermic mass loss at 509 °C, due to kaolinite dehydroxylation. For Al(III)TNMPC, there were two exothermic processes, at 471 and 507 °C, ascribed to aluminum(III) tetranitrometallophthalocyanine. As for KaPCNO₂, the kaolinite dehydroxylation temperature decreased (440 °C) as a result of PCNO₂ reacting with kaolinite. The temperatures at which exothermic Al(III)TNMPC degradation occurred increased because kaolinite conferred protection to the aluminum complex immobilized on the clay, consequently improving the thermal stability of the metallophthalocyanine.

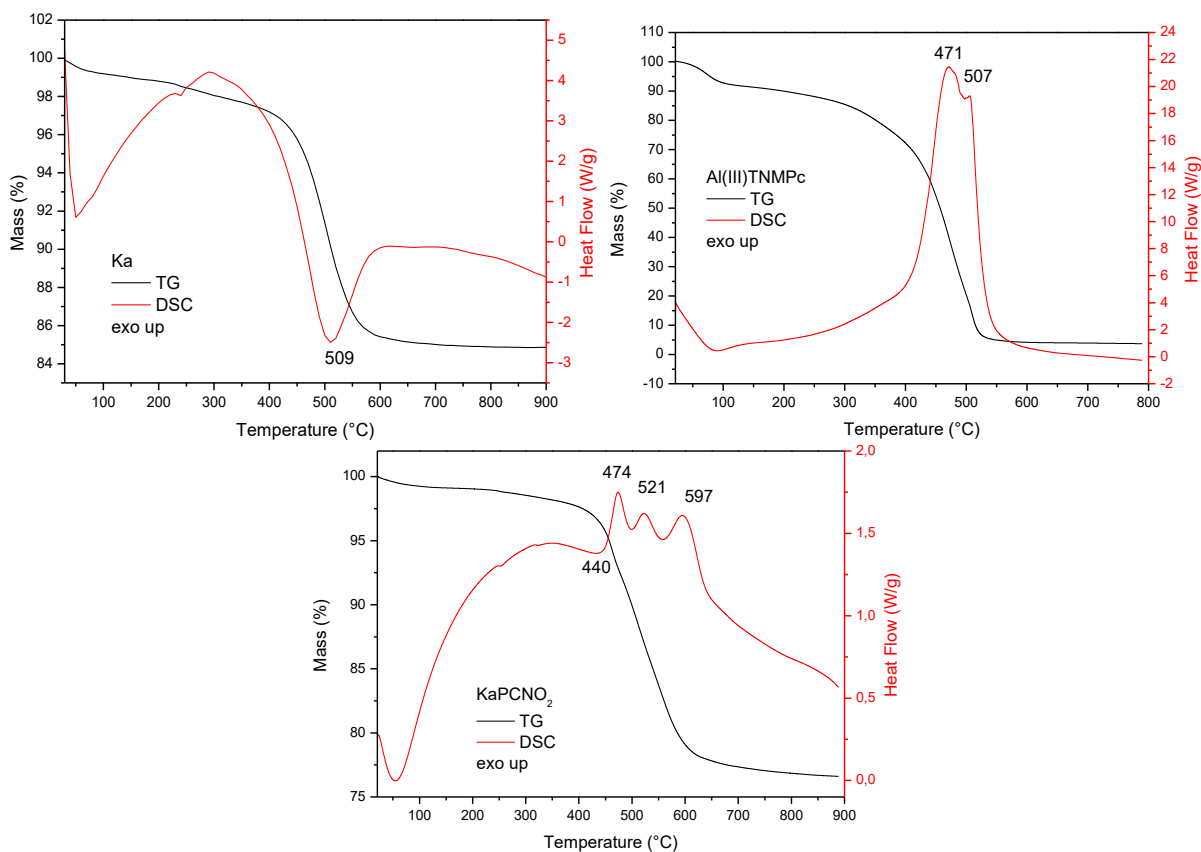


Figure III.7: TG/DTA curves obtained for Ka, Al(III)TNMPC, and KaPCNO₂.

²⁷Al NMR analysis

NMR is an important tool to characterize hybrid materials based on kaolinite. This technique evidences changes in the intensities and chemical shifts of octahedral (hexacoordinated) aluminum species, which are coordinated with reaction-prone hydroxyls present in the octahedral sheet (de Faria et al., 2009). Fig. III.8 shows the ²⁷Al NMR spectrum of KaPCNO₂.

The peaks with chemical shifts of 1.74 and 8.43 ppm were assigned to hexacoordinated (octahedral) aluminum in the kaolinite octahedral sheet (Fitzgerald et al., 1989; Letaief et al., 2006). Fitzgerald et al. (1989) demonstrated that the relation between octahedral and tetrahedral aluminum (relative intensities in the spectrum) was 400:1 for kaolinite. This was not the case for KaPCNO₂—the peaks due to tetrahedral aluminum were practically as intense as the peaks due to octahedral aluminum. Using an average value to calculate the ratio between octahedral and tetrahedral aluminum, the obtained ratio was approximately 1.4:1. These differences between kaolinite and the material synthesized herein may have stemmed from partial dissolution of aluminum present in the octahedral sheet during metallophthalocyanine synthesis, as judged from the chemical shifts at -67.99 and

84.85 ppm, due to tetracoordinated aluminum (Fitzgerald, J. John., 1989; Mantovani et al., 2011). Hence, free aluminum dissolved in the octahedral sheet might exist and participate in the phthalocyanine macrocycle cyclomerization, affording a metallophthalocyanine that bears aluminum as the central ion.

Lyubimtsev et. al. (2015) examined the reactivity of phthalonitriles derivatives containing different terminal groups to promote the phthalocyanine synthesis by conventional routes; for example, the 4-nitrophthalonitrile and 4-aminophthalonitrile, yielding results that demonstrate that the nitro group could influence the reactivity of the composite, the reaction rate is very bigger when use the derivative containing nitro group. Based on this theoretical and experimental result and based on the present study, we propose that by promoting the reaction of the 4-nitrophthalonitrile with kaolinite, it has the ability to dissolve partially the octahedral sheet of this clay mineral, inducing the leaching of Al^{3+} , consequently promoting the cyclomerization reaction without use conventional presence of metallic salts and solvents.

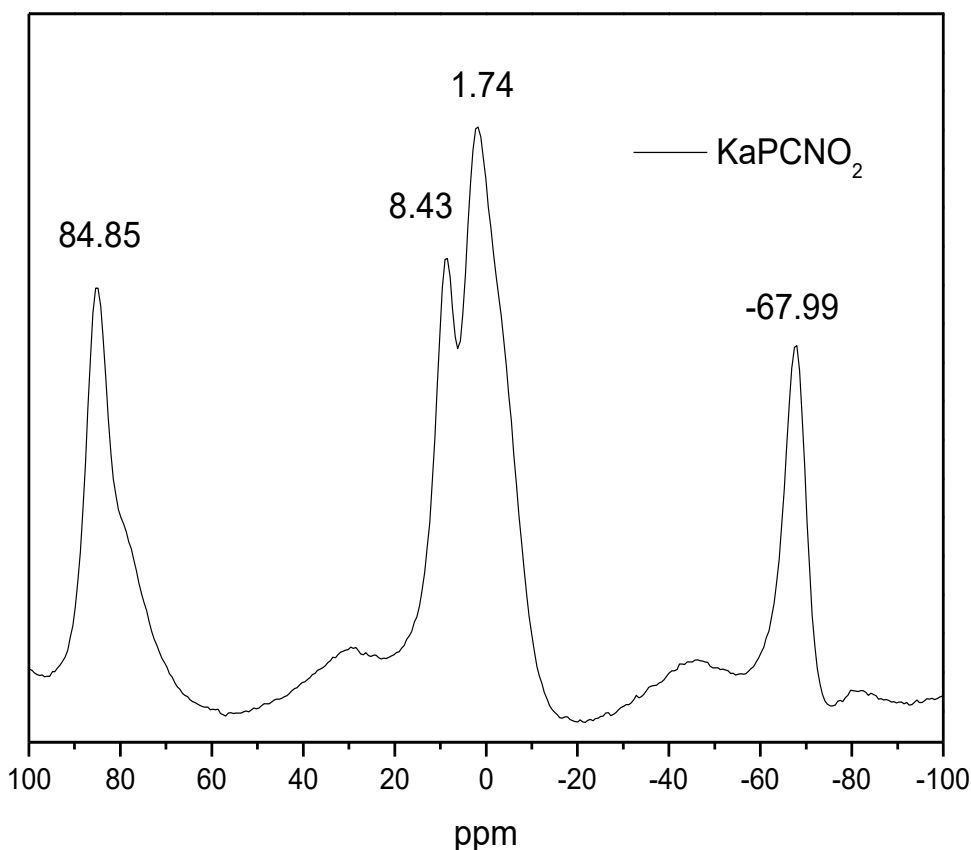


Figure III.8: ^{27}Al NMR spectrum of KaPCNO₂.

SEM analysis

SEM provided information about the morphology of the prepared materials. Fig. III.9 presents the SEM images obtained for KaPCNO₂ and Ka.

KaPCNO₂ was fragmented into poorly aggregated hexagonal sheets, forming a layered material with few pillared layers. Particles were smaller and less ordered as compared with Ka (Fig. III.9A and III.9B). These results agreed with XRD data and indicated that kaolinite was exfoliated/delaminated or even partially dissolved during metallophthalocyanine synthesis.

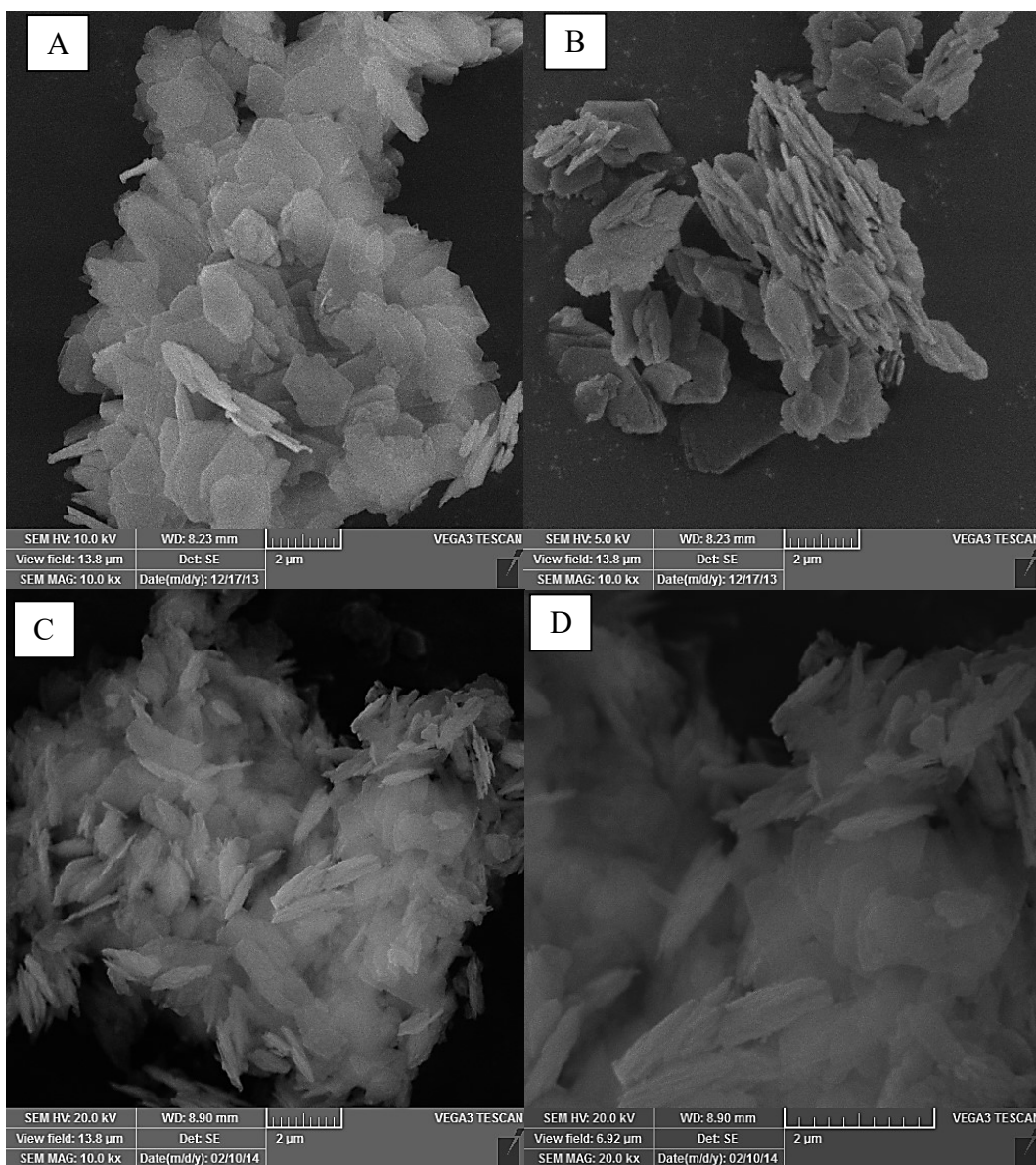


Figure III.9: SEM images of Ka (A and B) and KaPCNO₂ at 10kx (C) and 20kx (D) magnification

Mechanism Investigation

The analysis conducted in this study led us to propose a mechanism involving simultaneous metallophthalocyanine synthesis and immobilization on kaolinite. The stages of the proposed process are as follows (Fig. III.10 and III.11):

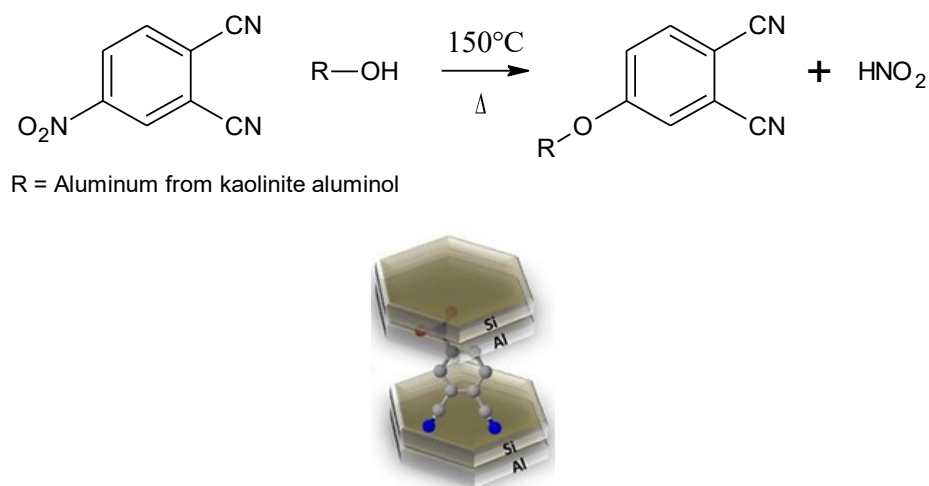


Figure III.10: Schematic representation of the first stage of in situ kaolinite-immobilized metallophthalocyanine synthesis

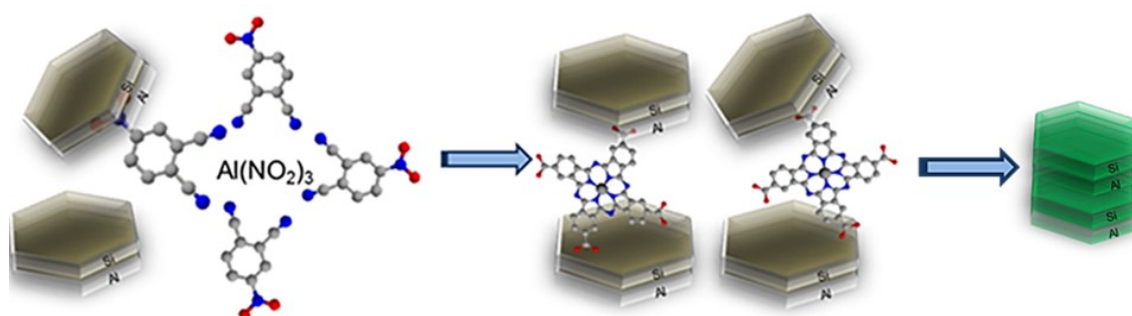
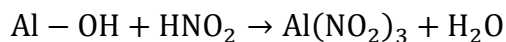


Figure III.11: Schematic representation of the third stage of in situ kaolinite-immobilized metallophthalocyanine synthesis.

1st stage: The nitro group of 4-nitrothalonitrile reacts with kaolinite, to functionalize part of the kaolinite lamellae with phthalonitrile and to generate nitrous acid as the reaction subproduct.

2nd stage: Nitrous acid reacts with nonfunctionalized aluminol, to dissolve part of the kaolinite octahedral sheets and to generate aluminum nitrite according to the following reaction:



3rd stage: For metallophthalocyanine synthesis to occur, it is necessary to add a metallic salt or a metal to the reaction medium. In the present case, addition of a metallic salt was dismissed because a salt originated in the reaction medium during the metallophthalocyanine synthesis. Indeed, the reaction medium contained kaolinite functionalized with 4-nitrophthalonitrile, nonfunctionalized kaolinite, 4-nitrophthalonitrile (added in excess), and aluminum nitrite (which emerged during the synthesis) (Fig. III.11). This mixture was kept at 150 °C for 48 h, to afford a green solid whose color was typical of metallophthalocyanine (see Fig. III.12)



Figure III.12: Kaolinite functionalized with aluminum(III) tetranitrometallophthalocyanine.

²⁷Al NMR and TG data attested to the synthesis of metallophthalocyanine catalyzed by kaolinite and reinforced our proposal that Al(III)TNMPC synthesis and immobilization occurred simultaneously. Indeed, the metallocomplex decomposed at higher temperature than the phthalonitrile precursor. The amount of metallophthalocyanine was calculated from the residue obtained from the thermogravimetric curve (Silva et al., 2012). The minimum formula based on the molar ratio Ka/Al(III)TNMPC was Ka-(Al(III)TNMPC)_{1.05}. The ratio between the intensities of the typical octahedral and tetrahedral aluminum chemical shifts was 1.4:1, which was completely different from the ratio observed for pure kaolinite (400:1). These results supported the hypothesis that Al(III) was partially removed from the gibbsite octahedral sheet, to induce formation of the aluminum(III) phthalocyanine. In other words, kaolinite served as support, catalyst, and source of Al(III) ions.

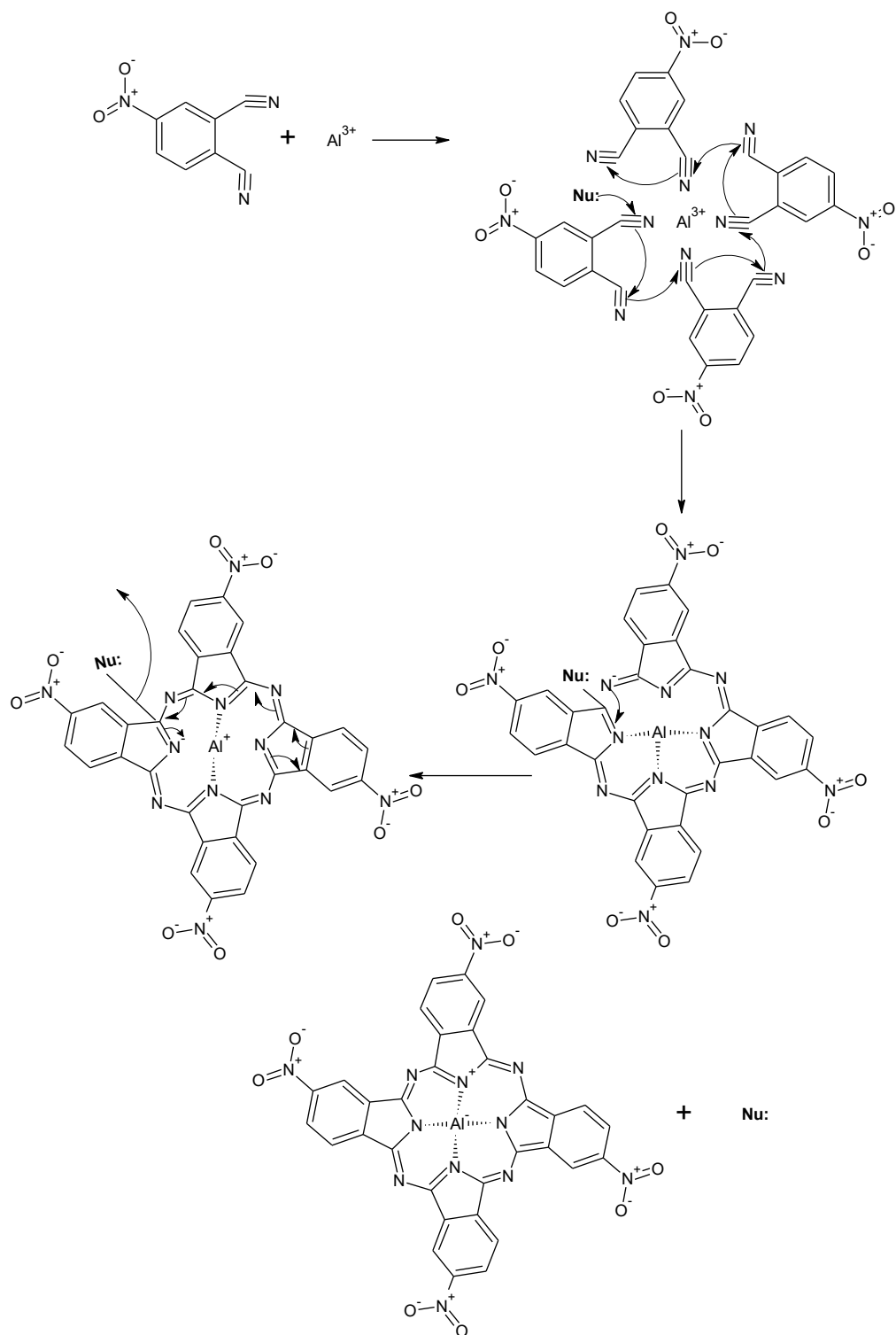


Figure III.13: Cyclization reaction mechanism for aluminum(III) metallophthalocyanine formation

The nitronium group is an intermediate state. The nitronium were generated from nitrosil groups from 4-nitrophthalonitrile precursor, when this specie attack the $\text{Al}(\text{OH})_3$ from gibbsite kaolinite layer. The possible mechanism, certainly involves the dissolution of

aluminium from kaolinite promoted by acidic attack of acid specie generated in situ, as represented in the scheme in Fig. III.13. The nitronium group (nucleophile) used at the start of the cyclization oxidizes nitrite to nitrate by donating two electrons to the macrocyclic complex. The resulting nitronium ions undergo aromatic electrophilic substitution at position 4 or combine with another nitronium ion, to produce a nitrogen molecule ($N_{2(g)}$). N_2 then participates in a substitution reaction, to form a nitrate monophthalocyanine and hydrogen gas.

Obviously the nitronium are not stable and could giving a rise to nitrite ion. This oxidation process could be probably induced by kaolinite wich contain many oxides such silicon oxide layer and aluminium oxide hydroxide layer and some impurities such as Ti, Fe and Mn oxides. It's importante remark that nitronium is one intermediate state and obviously at final we have presente only the nitrite ions.

Textural analysis

Specific surface area calculated by BET (Table III.2) shown that intercalation with DMSO and PCNO₂ grafting procedures to generate metallophthalocyanines induces a decreasing of the specific surface area, on other hand the pore size of the grafted compound Ka-PCNO₂ is bigger than for purified kaolinite (179 Å) with a value of 730 Å. In this sense the presence of large organic molecules such as Al(III)TNPMPC promotes the exposure of the interlayer hydroxyl groups inducing in all cases the decrease of specific surface area and increase of pore size, probably because the pores that were originated by intercalated DMSO molecules (anchored only by hydrogen bonds) into kaolinite structures were completely removed before PCNO₂ grafting. The changes in surface area values may be related to the stacking/restacking of kaolinite and Al(III)TNPMc complexes immobilization in situ and also to delamination of Ka-PCNO platelets that induces the textural changes of kaolinite.

Table III.2: Specific surface area (SBET) and pore size (VpTotal) using the BET method of kaolinite, kaolinite intercalated with DMSO and compound grafted with PCNO₂

Sample	$S_{BET} (m^2/g)$	Pore size (Å)
Ka	15,6	179
Ka-DMSO	4,2	806
Ka- PCNO ₂	0,3	729

Conclusion

FTIR, XPS and UV/Vis spectroscopy confirmed the one-step synthesis and immobilization of a metallophthalocyanine on kaolinite, with the clay serving as support/catalyst. XRD and SEM analyses showed that the kaolinite structure became disorganized during the synthesis. This disorganization was later confirmed by NMR—octahedral Al(III) ions dissolved in the reaction medium and promoted metallophthalocyanine cyclomerization in the presence of phthalonitrile. This process constitutes a new route for metallophthalocyanine synthesis that meets the principles of green chemistry and sustainability.

References for Article III

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CONCLUSÕES GERAIS

Nesta tese foi apresentado o desenvolvimento e estudo de novos materiais inorgânico-orgânicos aplicados a adsorção e processos fotocatalíticos e também novas rotas sintéticas na obtenção de materiais de interesse, como as metalofalocianinas. Segundo as atividades expostas, as principais conclusões do trabalho foram:

Artigo I: as técnicas de caracterização provaram que o dióxido de titânio e tetracarboxifalocianina de Co(II) foram imobilizados na caulinita; as reações ocorreram na superfície da caulinita, observando a influência da rota sintética (ácida e básica) nas propriedades texturais dos materiais obtidos; a quantidade de TiO₂ incorporado a caulinita foi maior na rota básica, devido a geração de cargas na superfície da argila, facilitando a imobilização; a rota ácida houve menor depósito de TiO₂ devido a geração de menos carga superficial. Frente aos estudos de fotodegradação, trimetoprim (30%) e prometrina (54%) apresentaram maior dificuldade no processo de degradação, já a cafeína apresentou elevada porcentagem de remoção (90%). A espectrometria de massa confirmou que houve a formação de subprodutos e/ou intermediários em todos os casos estudados. Com o estudo para a determinação do mecanismo de fotodegradação, observou-se que a degradação se dá principalmente mediante a geração do radical hidroxila, uma vez que houve a diminuição da porcentagem de degradação de 38 para 2,5%.

Como a cafeína é um marcador ambiental (e houve elevada porcentagem de degradação), sendo possível a presença de outros compostos orgânicos juntamente com a mesma, o estudo apresenta determinada relevância, pois pode ocorrer a degradação tanto da cafeína, quanto de outros compostos orgânicos que estejam no meio.

Vale ressaltar que nos processos estudados, não foram utilizados agentes oxidantes, como comumente é apresentado na literatura, tornado os resultados ainda mais relevantes frente à capacidade dos materiais obtidos serem capazes de gerar espécies que promovam a degradação de compostos orgânicos.

Artigo II: os materiais híbridos baseados em Laponita/3-cloropropiltriétoxissilano/Melamina ou Biureto foram obtidos com sucesso, utilizando duas rotas sintéticas (hidrolítica e não hidrolítica); as propriedades texturais e a presença dos grupos funcionais (Mel ou Biu) na superfície dos materiais são influenciadas pela rota sintética. No estudo de adsorção de TMP, o tempo necessário para atingir o equilíbrio quanto a capacidade de adsorção pode ser drasticamente influenciado pela rota sintética. Ajustes matemáticos foram aplicados para

compreender o processo de adsorção, sendo que os materiais se ajustam melhor no modelo de pseudo-primeira ordem, evidenciando que o processo de adsorção ocorre por fisissorção, e ao modelo matemático de Sips, que é a combinação dos modelos de Langmuir e Freundlich.

Artigo III: o material híbrido baseado em caulinita/metalofalocianina foi obtido em uma única etapa, síntese e imobilização; a confirmação da obtenção e imobilização da MPC em caulinita se deu pelas técnicas de FTIR, XPS e UV/Vis, observando bandas características da MPC, principalmente por XPS. A caulinita apresentou-se desorganizada, pois ocorreu o processo de dissolução parcial dos íons de Al(III) hexacoordenados (octaédricos), comprovado por RMN ^{27}Al , pois a relação entre alumínio octaédrico e tetraédrico diminuiu de 400:1, na caulinita, para 1,4:1; o alumínio “livre” dissolvido participar na síntese da ftalocianina, resultando em uma metalofalocianina com o alumínio como íon central.

PERSPECTIVAS

A tese desenvolvida abre possibilidades na obtenção de novos materiais, compósitos ou híbridos, que sejam multifuncionais e que tenham propriedades específicas, mediante desenvolvimento de:

- Novos catalisadores e fotocatalisadores baseados em matrizes inorgânicas complexadas com macromoléculas orgânicas, para suprir dificuldades e desvantagens da utilização de dióxido de titânio;
- Utilização de radiação visível (natural ou artificial) para utilização de metalofalocianinas como agentes de transferência de energia (efeito antena) para semicondutores.
- Diferentes rotas sintéticas de imobilização de moléculas de interesse, para obtenção de materiais aplicados à adsorção/dessorção, catálise/fotocatálise baseados em diversos argilominerais naturais e sintéticos, com reações superficiais ou no espaçamento basal;
- Produção de metalofalocianinas por rotas sintéticas alternativas, utilizando argilominerais como reagentes doadores de íons metálicos, e sua consequente imobilização, diminuindo etapas no processo sintético de híbridos orgânico-inorgânico.

CONCLUSIONES GENERALES

Esta tesis presenta el desarrollo y estudio de nuevos materiales inorgánicos-orgánicos aplicados a procesos de adsorción y fotocatalíticos y también nuevas rutas sintéticas para obtener materiales de interés, como las metalofalocianinas. Según las actividades expuestas, las principales conclusiones del trabajo fueron:

Artículo I: las técnicas de caracterización han probado que el dióxido de titanio y la tetracarboxifalocianina de Co(II) fueron inmovilizados en la caolinita; las reacciones ocurrieron en la superficie de la caolinita, observando la influencia de la ruta sintética (ácida o básica) en las propiedades texturales de los materiales obtenidos. La cantidad de TiO_2 incorporado a la caolinita fue mayor en la ruta básica, debido a la generación de cargas en la superficie de la arcilla, facilitando la inmovilización. La ruta ácida produjo una menor fijación de TiO_2 debido a la generación de menos carga superficial. En los estudios de fotodegradación, el trimetoprim (30%) y la prometrina (54%) presentaron mayor dificultad de degradación, mientras que la cafeína presentó un elevado porcentaje de eliminación (90%). La espectrometría de masas confirmó la formación de subproductos y/o intermediarios en todos los casos estudiados. Analizando el mecanismo de fotodegradación se encontró que se produce principalmente mediante la generación del radical hidroxilo, una vez que el porcentaje de degradación disminuyó de 38 a 2.5%.

Dado que la cafeína es un marcador ambiental (y hubo un alto porcentaje de degradación), y la presencia de otros compuestos orgánicos junto con ella es posible, el estudio tiene cierta relevancia, ya que puede haber degradación tanto de la cafeína como de otros compuestos orgánicos que están presentes en el medio.

Es de destacar que en los procesos estudiados, no se utilizaron agentes oxidantes, como se presenta comúnmente en la literatura, lo que hace que los resultados sean aún más relevantes dada la capacidad de los materiales obtenidos para poder generar especies que promueven la degradación de los compuestos orgánicos.

Artículo II: Se obtuvieron con éxito materiales híbridos basados en Laponita/3-cloropropiltriétoxilano/Melamina o Biuret, utilizando dos rutas sintéticas (hidrolítica y no hidrolítica). Las propiedades texturales y la presencia de dos grupos funcionales (Mel o Biu) en la superficie de los materiales vienen determinadas por la ruta sintética. En la adsorción de trimetoprim, el tiempo necesario para alcanzar el equilibrio también depende drásticamente de la ruta sintética. Se utilizaron ajustes matemáticos para comprender el proceso de adsorción, el cual se ajusta mejor al modelo de pseudo-primer orden, evidenciando que está condicionado por la fisorción, y al modelo de Sips, que es una combinación de los modelos de Langmuir y Freundlich.

Artículo III: Se obtuvo un material híbrido basado en caolinita/metalofalocianina en una única etapa de síntesis e inmovilización. La confirmación del proceso se obtuvo por las técnicas de FTIR, XPS y UV/Vis, observando bandas características de MPC, principalmente por XPS. La caolinita apareció desorganizada, debido a la disolución parcial de cationes Al(III) hexacoordinados (octaédricos), comprobado por RMN de ^{27}Al ; la relación entre aluminio octaédrico y tetraédrico disminuyó de 400:1 en la caolinita hasta 1,4:1. El aluminio “libre” disuelto de la capa octaédrica puede participar en la síntesis de la ftalocianina, dando lugar a una metalofalocianina con aluminio como catión central.

PERSPECTIVAS

La Tesis de Doctorado realizada abre nuevas posibilidades en la obtención de nuevos materiales, compuestos o híbridos, que sean multifuncionales y que tengan propiedades específicas, mediante el desarrollo de:

- Nuevos catalizadores y fotocatalizadores basados en matrices inorgánicas complejadas con macromoléculas orgánicas, para salvar las dificultades y las desventajas de la utilización del dióxido de titanio.
- Utilización de radiación visible (natural o artificial) en el uso de metalofalocianinas como agentes de transferencia de energía (efecto antena) en semiconductores.
- Diferentes rutas sintéticas de inmovilización de moléculas de interés para la obtención de materiales aplicados en adsorción/desorción y en catálisis/fotocatálisis basados en diversos minerales arcillosos naturales y sintéticos, mediante reacciones en su superficie o en su región interlamina.
- Producción de metalofalocianinas por rutas sintéticas alternativas, utilizando minerales arcillosos como reactivos dadores de cationes metálicos, con su inmovilización consecuente, disminuyendo las etapas del proceso sintético de materiales híbridos orgánico-inorgánicos.