

Development of a New Adsorbent Material for Removing Corrosive Metallic Ions Presents Automotive Fuels

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ABSTRACT

The compound of calcium phenylphosphonate (CaPP) was prepared and intercalated with *m*-aminobenzoic acid (MABA), resulting in compound CaPP/MABA. These materials were characterized by nitrogen elemental analyses, X-ray diffraction, infrared spectra, thermo gravimetric analysis, ¹³C nuclear magnetic resonance and scanning electron microscopy. Then the surface of the compound CaPP/MABA were absorbed metallic ions Cu(II) and Zn(II), forming lamellar metalized complexes (CaPP/MABA/Cu(II) and CaPP/MABA/Zn (II)).

Keywords: intercalation, adsorption, characterization.

INTRODUCTION

In the solid state there are many compounds that exhibit the properties of lamellar inorganic structures or two-dimensional materials, which are characterized by the fact that the atoms that constitute are bonded covalently way, an organized arranged to form layers or lamellae. In some of these materials, these layers are electrically neutral and are joined together by weak interactions van der Waals type. Thus, the lamellae are maintained by interlayer forces that have weaker bonds existing between the atoms present in the lamella, causing a strong anisotropy to the material. This fact allows species such as ions, atoms or molecules enter the interlayer space, such phenomenon is known as intercalation [1].

In the intercalation reactions the substances involved are treated as guests and the receptor matrix are called host. In these reactions, the occupation of the interlayer space of a material allows the occupation of a guest species as ion, atom or molecule, which process can be described by Equation 1:



where: C is the guest species, $\square yH$ is the host matrix, \square are empty sites of the host matrix, $Cx\square y-x H$ is the host matrix containing x sites, previously empty, occupied by guest species,

thereby forming the compound of intercalation. As can be seen from equation 1, empty sites of lamellar materials can or can not be fully occupied by the guest species, opening the possibility of formation of non-stoichiometric compounds. It should be emphasized that equation 1 is a schematic representation of an intercalation reaction, where the interlayer space is indicated in the host matrix as an empty reticular site. In fact, these sites are not represented and the equation 1 would be simplified as:



The intercalations are usually accompanied by an increase in the interlayer distance of the host matrix so that to provide a perfect accommodation of guest type, and this distance can be calculated by subtracting the value of the interlayer distance of the material intercalated by the distance value of the compound of origin [1,2].

The energetic cost involved in the separation of the lamellae is compensated by additional stability resulting from interactions between the host and the guest in forming the final compound.

The interest in intercalation reactions is based precisely on the fact that the intercalated molecules modify the properties of the resulting compound. Thus, by X-ray diffraction it is

possible to accompany an intercalation reaction, monitoring the variation of the interlayer distance when successive entrance guest species, which can be perfectly followed by the displacement of the peak of the plane of the lamellae. In compounds of lamellar structure, the peak that occurs at smaller values of angles 2θ correspond to the distance between the planes of the lamellae. With the intercalation, it occurs a weakening of the interactions between the lamellae, due to the increased distance between them, so that displacement occurs in a new position of equilibrium, with a consequent formation of new diffraction planes [1-3].

The characterization of intercalation compounds is one of the major challenges in this area and it is essential for their development, not only in respect to properties as well as to applications of such systems.

The phenylphosphonates intercalated with organic compounds have attracted interest since they can act as ligands for the coordination of metallic ions on their surface and to be used in the construction of chemically modified electrodes (CME), along with carbon paste electrode (CPE), in the study of the electrochemical behavior of these compounds in electro analysis and electro catalysis [4-7] and also the adsorption and pre-concentration of metallic ions from ethanol solutions [8].

The present investigation deals with the synthesis, characterization, and adsorption properties of layered calcium phenyl phosphonate intercalated with m-amino benzoic acid. As the guest molecule contains nitrogen and oxygen atoms from amine and carboxylic groups, these basic centers are potentially useful for cation coordination in ethanol solution, an aspect that is also explored in this study.

EXPERIMENTAL

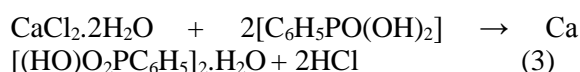
Materials

Reagent grade chemicals and deionized water were used throughout the experiments. Phenylphosphonic acid, (Aldrich), calcium chloride (Merck), sodium hydroxide (Vetec), zinc chloride (Vetec) and copper chloride (Vetec) were employed in all preparations.

Synthesis of Calcium Phenylphosphonate

Layered calcium phenylphosphonate was synthesized as described elsewhere [9]. Briefly, 60.0 cm³ of a 1.0 mol dm⁻³ aqueous solution of phenylphosphonic acid was reacted with 25.0 cm³ of 0.50 mol dm⁻³ of dehydrated calcium

chloride. To this mixture, 1.0 mol dm⁻³ of sodium hydroxide was added dropwise under vigorous magnetic stirring to adjust the pH from 5 to 6. The reaction is given by equation 3.



Calcium phenylphosphonate immediately settled down as an abundant white solid and it was isolated by filtration, washed with double-distilled water, and air dried at 320 K.

Intercalation Procedure

About 20 mg of calcium phenylphosphonate were immersed in 20.0 cm³ of 1.0x10⁻³ mol dm⁻³ ethanolic m-aminobenzoic acid and the suspension was shaken in an orbital mechanical stirrer for 1 h. This time was determined for a constant concentration of m-aminobenzoic acid by varying the solid/solution contact time up to 12 h in order to obtain the best intercalation condition for this guest molecule. The resulting solid was filtered, washed with doubly-distilled water, and dried at room temperature. Two kinds of host-guest compounds were obtained and abbreviated as CaPP/MABA.

Characterization

Calcium and phosphorus [10, 11] elemental analyses were performed by atomic absorption spectroscopy using a Perkin Elmer atomic absorption spectrometer, model 5100, and spectrophotometric methods using a Shimadzu spectrophotometer, model MultiSpec-1501.

The amount of m-aminobenzoic acid intercalated into calcium phosphate was determined by nitrogen elemental analysis on a Perkin-Elmer Analyzer 2400 series H CHNS/O apparatus.

X-ray diffraction patterns were obtained with nickel-filtered CuK α (0.154 nm) radiation in the interval of 2 to 65 $^\circ$ at a speed of 0.033 $^\circ$ s⁻¹ and a step of 0.050 $^\circ$ on a Shimadzu XD3-A diffractometer (30/20 kV/mA).

Infrared spectra of the samples were acquired on a Perkin-Elmer FTIR spectrophotometer, model 1600, by using pressed KBr pellets in the 4000-400-cm⁻¹ range with 4 cm⁻¹ of resolution.

Thermogravimetric curves were recorded using a DuPont model 1090 B apparatus coupled to a model 951 thermobalance, by heating samples from room temperature to 1273 K at a heating rate of 0.16 K s⁻¹ in an argon flow of 1.67 cm³ s⁻¹. The samples varied in weight from 15.0 to 30.0 mg.

The nuclear magnetic resonance spectra of the solid material were obtained on an AC 300/P Bruker spectrometer at room temperature at 75.5 MHz. A pulse repetition time of 3 s and contact time of 3 ms were used.

Scanning electron microscopy (SEM) images were obtained for samples dispersed on a double-faced conducting tape adhered to an aluminum support. The samples were coated with gold using a Balzer MED 020 low-voltage sputtering apparatus. The measurements were carried out on a JEOL JSM-T300 scanning electron microscope.

Adsorption isotherms

The adsorption isotherms for ZnCl₂ and CuCl₂ in ethanol solutions were performed by using the batchwise method. For each isotherm, a series of samples containing 100 mg of CaPP/MABA was shaken for 2 h, as previously established, in a orbital bath with variable concentrations of each metal halide at a constant temperature of 298 ± 1 K. The concentration of the metal ion in solution in equilibrium with the solid phase was determined by direct titration with EDTA (0.010 mol dm⁻³) using murexide and eriochrome black T as indicator. The amount of cations adsorbed, n_f, was determined by applying the equation: n_f = (n_a - n_s)/m, where m is the mass of the adsorbent and n_a and n_s are the initial and the equilibrium amounts of the metal in the solution phase in number of moles, respectively, which is a measure of the degree of coverage for each of the experimental conditions used, i.e.

$$n_f = \frac{n_a - n_s}{m} = \sum_m \frac{[(CaPP/MABA)_m MCl_2]}{m} \quad (4)$$

where the summation extends over all species on the surface. The maximum number of moles of the adsorbed complex n_f^{max} is equal to the maximum value n_f when the concentration of Cu (II) and Zn (II) tends to infinity.

Adsorption of Cu (II) and Zn (II) contained in solution depends on the selectivity coefficients of the complexes formed with the ligand immobilized on the surface. The formation of the equilibrium of the complex Cu(II) and Zn(II) with CaPP/MABA were studied on the Filippov model [12,13].

The reaction of complex formation at the surface can be generically represented by equation 5:



where z is the charge of the metallic ion, X is an anion with charge unit and R is a linking group, electrically neutral, fixed on the support surface. For equilibrium (6), it is applied a relation of the type:

$$\theta_n/(1-\theta_n) = \gamma_n C \quad (6)$$

where the fraction of CaPP/MABA bonded to metal is $\theta_n = \tilde{n} n_f/n_0$, being n₀ the quantity of MABA intercalated in CaPP (mol g⁻¹), \tilde{n} is the number of ligands bonded to the metal, and γ_i is the stability constant. Substitution in the preceding equation results in the final expression [13,14]:

$$\frac{1}{n_f} = \frac{\tilde{n}}{C_N \gamma_n C} + \frac{\tilde{n}}{C_N} \quad (7)$$

Considering that the metallic ions Cu(II) and Zn(II), when adsorbed on the surface (with a homogeneous covering ligands) it forms immobilized complexes with different ratios between it and the CaPP/MABA anchored, the total concentration of immobilized ligand on the surface is equal to the sum of the concentrations of all species; (\tilde{n}) average number of supported ligands bound to a metallic ion will be:

$$\tilde{n} = \frac{[MRX_z] + 2[MR_2X_z + \dots + m[MR_mX_z]}{n_f} \quad (8)$$

Equation 7 can be written:

$$\frac{1}{n_f} = \frac{\tilde{n}}{C_N \Gamma_n C} + \frac{\tilde{n}}{C_N} \quad (9)$$

which Γ_n is the selectivity coefficient equal to $\sum_{m=1}^n Y_m$

RESULTS AND DISCUSSION

Characterizations

Based on the elemental analysis results of 10.1, 15.6, 37.2 and 3.0 % calcium, phosphorus, carbon and hydrogen the amounts of 10.25, 15.90, 36.96 and 3.12 mmol g⁻¹ were calculated, respectively. Based on these results it is proposed the following molecular formula Ca(HO₃PC₆H₅)₂·2H₂O.

The quantity of m-aminobenzoic acid intercalated into calcium phenylphosphonate was determined through 4.5 % of nitrogen atoms of this guest molecule, which corresponds to 3.2 mmol g⁻¹.

A proposed intercalation scheme for m-aminobenzoic acid inside the free inorganic host cavity is shown in **Figure 1**.

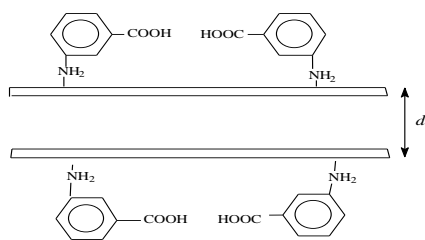


Figure1. Schematic representation of calcium phenylphosphonate intercalated with *m*-aminobenzoic acid.

The X-ray diffractogram provides the angle between the incidence of the diffracted radii and the sample (2θ) still showing the relative intensity. The technique is non-destructive and only small amount of powder sample is sufficient for the identification of the crystal phase present. Through the Bragg equation,

$$2d \sin\theta = n\lambda \quad (10)$$

where $\lambda = 1.5406 \text{ \AA}$ is the wavelength of the radiation used, it is possible to determine the distance interlayer d (\AA) between the atomic planes of the crystal lattice.

The high degree of crystallinity of the calcium phenylphosphonate compound reflects in well-formed X-ray diffraction powder patterns, showing the presence of a sharp and intense peak attributed to the 001 plane, with an interlayer spacing that corresponds to 2θ value of 5.92° , giving a basal distance of 1494 pm, [15] as illustrated in **Figure 2a**. As expected, this distance increases when the inorganic support is suspended in ethanolic solution containing dissolved MABA guest molecule, to give, in the present case, a sharp peak at $2\theta = 5.52^\circ$, which corresponds to an interlayer distance of 1601 pm, as illustrated in **Figure 2b**, an increase of 107 pm in comparison to that of the original host, showing that the intercalation occurs exclusively on the external surface of the inorganic support (**Figure 1**).

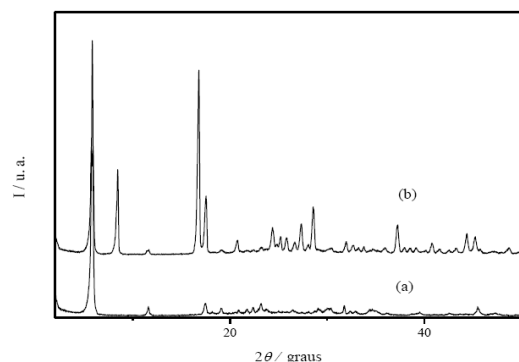


Figure2. X-ray diffraction of calcium phenyl phosphonate (a) and the respective intercalated compound with *m*-aminobenzoic acid (b).

The infrared spectra of these compounds gave important features related to the presence of water bonded to the inorganic layer, as shown in **Figure3**, which contains attached organophosphate groups. A weak and broad band at 3500 cm^{-1} may be assigned to the OH vibration, which may be associated with the organophosphate group directly bonded to the inorganic layer and to the presence of water, which enhances due to easy absorption during the manipulation process of the sample [16]. The weak band at 1438 cm^{-1} and the medium bands in the $(720 \text{ to } 694) \text{ cm}^{-1}$ range indicate the presence of phenyl rings and the bands that appear at $(1080, 1017 \text{ and } 996) \text{ cm}^{-1}$ are due to PO_3 groups. Three bands are related to the ring, two of them weak, in the $(3000 \text{ to } 2830) \text{ cm}^{-1}$ region, and one at 1437 cm^{-1} , corresponding to the symmetrical and asymmetrical C-H stretching and to the C-C stretching C-C band of the ring respectively [17]. The band at 1250 cm^{-1} is assigned as the out-of-plane deformation of the P-OH groups [18], indicating the existence of remaining unreactive groups during compound formation, which act as acidic site in the lamella. In general, when interactions occurred, this band did not disappear, but decreased in intensity, indicating a partial acidic center saturation by the amines. In the spectrum of calcium phenylphosphonate intercalated with *m*-aminobenzoic acid (**Figure 3b**) is not possible to verify the presence of bands attributed to vibrations of N-H and other bands of the inorganic matrix few changes suffered the intercalation.

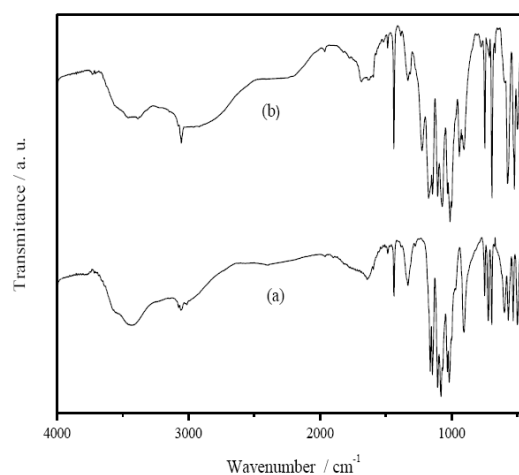


Figure3. Infrared spectra of calcium phenylphosphonate (a) and intercalated with *m*-aminobenzoic acid (b).

The thermogravimetric curves for calcium phenylphosphonate and that containing *m*-aminobenzoic acid intercalated are shown in **Figure 4**. The thermal decomposition of

calcium phenylphosphonate intercalated with m-aminobenzoic acid exhibits similar decomposition mechanism of the original compound. There are differences in the percentages lost in the first temperature stage, which are always higher 5.2%, since the acid out with water [19]. The following processes were detected: i) water molecule loss from room temperature to near 570 K; ii) loss of the intercalated molecule from 583 up to 720 K, and iii) two steps due to the loss of phenyl groups [20] in the ranges of 720-900 K and 980-1270 K, respectively, to yield $\text{Ca}(\text{PO}_3)_2$ [21].

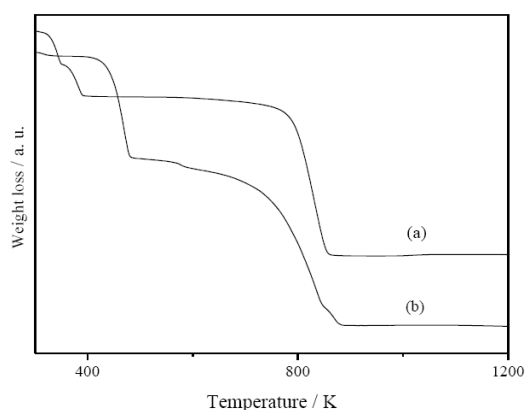


Figure 4. Thermogravimetric curves of calcium phenylphosphonate (a) and intercalated with 4-aminobenzoic acid (b).

An unequivocal confirmation about the phenylphosphonate group attachment on the inorganic structural layer is provided by a ^{13}C MAS NMR spectrum of the bonded phenylphosphonate, as shown in **Figure 5**, in which the structured carbon atoms on the ring are numbered as shown in the inserted phenyl structure. The assignments for the sequence of carbon atoms were proposed previously [22]. Thus, the series of peaks at 140, 138, 128 and 123 ppm, correspond to C^1 , C^2 and C^6 , C^4 , C^3 and C^5 , respectively.

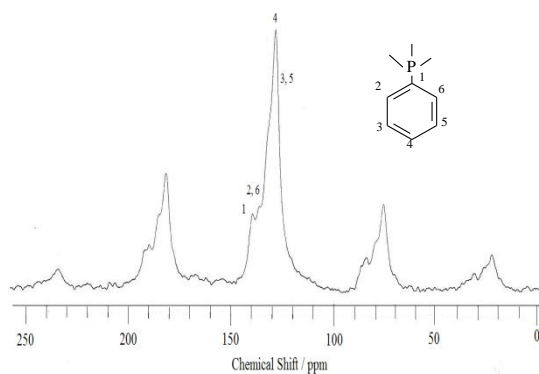


Figure 5. ^{13}C MAS NMR spectra of calcium phenylphosphonate.

The scanning electron microscopy photographs for calcium phenylphosphonate intercalated with m-aminobenzoic acid is shown in **Figure 6**. The crystal morphology of these compounds is clearly lamellar, which is in good agreement with the expected structural characteristics. The morphology of intercalated m-aminobenzoic acid is much similar to that of the host matrix. These results are very important in order to obtain pillared compounds with a high degree of crystallinity.

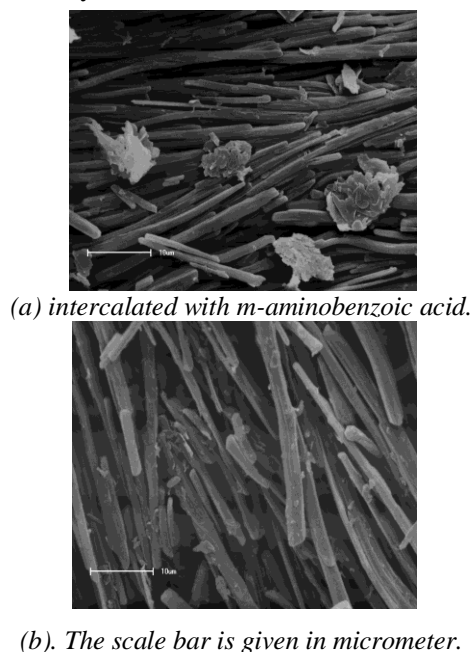


Figure 6. Scanning electron microscopy photographs of calcium phenylphosphonate.

Adsorption Isotherms

Taking into account the use of the intercalated crystalline lamellar compound in metal ion adsorption from ethanol solutions, the corresponding isotherms of the selected cations, Cu^{2+} and Zn^{2+} , were investigated. Preliminary investigation demonstrated that the original matrix does not adsorb these cations. The adsorption isotherm of both cations by CaPP/MABA is shown in **Figure 7**.

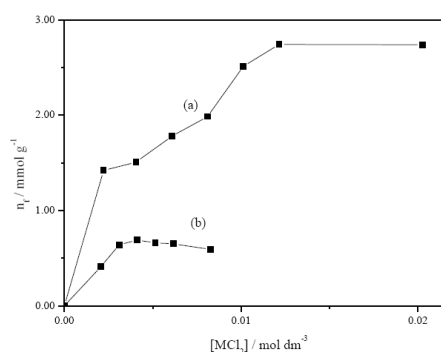


Figure 7. Isotherms of copper (a) and zinc (b) adsorption on the intercalated compound.

The solid adsorption capacity of metal halide on CaPP/MABA depends on the nature of the complex formed on the surface and the affinity of any particular attached ligand for the metal. In the present case, the maximum adsorption capacity, n_f^{\max} , for CuCl_2 and ZnCl_2 , was 2.74 and 0.66 mmol g^{-1} , respectively, indicating that copper binds more effectively than cobalt to the available basic centers. This sequence is the opposite of that of hydrated cation size [23], 147.8 and $169.6 \text{ cm}^3 \text{ mol}^{-1}$ for divalent copper and zinc, respectively. Supposing that the same behavior occurs in ethanol, these values suggest that during the complex formation, the cation-basic center interaction is favored for the less solvated cation at the solid/liquid interface. On the other hand, as the cation was solvated, the restriction to enter the lamellar space increased, disfavoring the bond to the basic center [24], and the pendant benzene group attached to the inorganic layer also restricted the mobility of the cation for binding. The average stability constant (Γ) and the average number of ligands bonded and coordinated to the metallic ion (\bar{n}) were determined from the plot of $1/n_f$ and $1/C$. The average stability values of CuCl_2 and ZnCl_2 in CaPP/MABA were 158 and $887 \text{ dm}^3 \text{ mol}^{-1}$, respectively, and the average number of ligands (\bar{n}) for CaPP/MABA were two and four to copper and zinc metallic ions. The values of the calculated constants indicate the formation of a stable complex.

CONCLUSION

The lamellar properties presented by the crystalline compounds calcium phenylphosphonate can accommodate the *m*-aminobenzoic acid into its interlamellar space. The intercalation process gave results indicating that the acidic centers of the inorganic layers were partially saturated, as indicated for the P-OH groups by infrared spectroscopy and for the original interlamellar distance of the matrix by X-ray diffraction patterns. The weight loss by thermal decomposition of intercalated consist species of the following stages: loss of the amines and water molecules, loss of the organic molecules and loss of the phenyl groups. However, during the intercalation processes the layered crystal structure of these inorganic matrices is essentially maintained. The availability of the basic centers in the intercalated compound gives this material the property of adsorbing cations from ethanol solution at the solid/liquid interface, a behavior that may be useful in cation removal.

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