

Fibrous Cerium (IV) Acid Phosphates Host of Weak and Strong Lewis Bases

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Abstract

In this paper, we evaluated the behavior of fibrous cerium (IV) acid phosphate (CeP) in insertion procedures involving a strong Lewis base (ethylamine) and a weak one (ϵ -caprolactam). In the former case, the procedure was performed by exposing a sample of CeP to a saturated amine atmosphere. Insertion was shown to be independent of the crystallinity of CeP, and the products showed strong host–guest interactions of the Coulombic type. Conversely, ϵ -caprolactam insertion was achieved by immersing CeP samples into its fused form. This process was dependent on the crystallinity of the inorganic solid, and host–guest interactions were characterized as involving hydrogen bonds.

Introduction

Cerium (IV) acid phosphate (CeP) belongs to the class of acid phosphates of tetravalent metals (APTMs). Very usually the APTMs present layered structures, as characterized for zirconium (IV) hydrogenphosphate by Clearfield and Smith [1], and recently, for germanium hydrogenphosphate by our research group [2].

Many publications have reported about CeP [3–16]. The efforts directed toward its preparation and physical characterization were initiated at the beginning of the sixties and have rapidly expanded. First obtained in its amorphous form, crystalline samples were also synthesized showing different degrees of lattice ordering and morphologies varying from polycrystalline powder to fibrous self-supported sheets [3–16]. It was verified that preparation methods and reaction conditions strongly influence the composition, and morphology of CeP, evidencing that many kinds of CeP may be obtained just varying P/Ce molar ratio of the starting reagents, as well as the time and temperature of reaction [5–7]. Reaction parameters also influence the physicochemical properties of the resultant material. In addition, the structure of CeP samples remains unknown due to their lack of crystallinity avoiding any satisfactory structure refinement.

CeP was the first acid salt of a tetravalent metal prepared with fibrous morphology [4, 6, 16], a suitable property from the practical point of view since flexible self-supported sheets, similar to cellulose paper, may be obtained through simple filtration of its aqueous sus-

pension. This property, allied with their porous structure showing acidic hydrogen atoms, made the CeP crystalline forms useful as inorganic ion-exchanger papers [5].

The possibility of obtaining flexible sheets of CeP and the presence of the highly oxidative Ce (IV) ions provided conditions for obtaining organo-inorganic hybrids by means of *in situ* oxidative polymerization. Verissimo and Alves [16] developed a new organo-inorganic nanocomposite conductor by reacting self-supported fibrous CeP sheets with pyrrole. Pyrrole molecules were polymerized on the surface of the CeP nanofibers, giving rise to a polypyrrole coating. However, the interstitial region of the CeP matrix was not explored since polypyrrole was formed more rapidly than the pyrrole monomers could diffuse into this region.

We believe that a series of additional organo-inorganic nanocomposites involving self-supported CeP sheets may be obtained by means of the insertion of less oxidative monomers followed by *in situ* polymerization. Exchangeable interstitial acidic hydrogen atoms promote the driving force, which enables insertion reactions between Lewis bases and CeP. However, as far as we know, insertion processes are issues almost completely unexplored for fibrous CeP.

In this work we concentrate on elucidative studies about the insertion properties of fibrous CeP. For this purpose, processes involving a strong and a weak Lewis base, namely ethylamine and ϵ -caprolactam, were performed in order to give information related to the dependence of insertion on to the crystallinity of CeP as

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well as about the nature of the host–guest interactions shown by the insertion compounds.

Experimental section

Materials

All chemicals were used without further purification. Ammonium cerium (IV) nitrate and phosphoric acid (85%) were obtained from Merck. Ethylamine solution (70%) and ϵ -caprolactam (99%) were obtained from Riedel-de Hen and Aldrich, respectively.

Preparations of CeP samples

Previous studies performed by Verissimo and Alves [16] on the preparation of self-supported sheets of CeP were adopted in this work. In a typical procedure, 300 cm³ of phosphoric acid (85%) was added dropwise to a round-bottomed flask containing 300 cm³ of a 0.05 mol dm⁻³ ammonium cerium (IV) nitrate aqueous solution. The mixture was then kept under magnetic stirring and heating. The temperature and time of heating were used to control the crystallinity of the CeP samples. The sample prepared through heating at 70 °C for 4 h was named CeP70-4. Another sample, named CeP90-4 was obtained after 4 h of heating at 90 °C. After the reaction time was complete, the solids were isolated by centrifugation and thoroughly washed with water. The solid was then redispersed in distilled water and filtered in a Buchner funnel. CeP self-supported sheets were obtained after air-drying the solid adhered to the membrane.

Insertion of ethylamine

Ethylamine insertion was performed by exposing CeP samples to a saturated atmosphere of the amine for 48 h. Amine that was not occluded was removed by drying samples under dynamic vacuum for 6 h.

Insertion of ϵ -caprolactam

CeP samples were immersed in fused ϵ -caprolactam (m.p. 69–72 °C) for approximately 15 s and then air dried. Not occluded lactam adhered onto the surface of the sheets was removed by heating them at 80 °C under dynamic vacuum for 6 h.

Analytical procedures

The ³¹P nuclear magnetic signal spectra with magic angle spinning (³¹P MAS NMR) were obtained at 202.35 MHz on a Varian Inova 500 spectrometer at 4.0 kHz. Chemical shifts were determined with respect to an external standard of H₃PO₄. The P/Ce molar ratios of CeP samples were determined by induced coupled plasma optical emission spectrometry (ICP) on

a Perkin Elmer Optima 3000DV apparatus. Calibration curves were constructed by standard procedures using aqueous solutions of cerium (IV) sulfate and potassium dihydrogenphosphate with several concentrations. X-ray diffraction (XRD) measurements were performed on a Shimadzu XRD-6000 powder diffractometer using Cu K_α radiation. FTIR spectra were obtained on a Bomem MB-series spectrometer. Samples were prepared as ‘Fluorolube’ mulls. Raman spectra were recorded on a Renishaw Raman Imaging Microprobe 3000 system, using a He-Ne laser (632.8 nm) as excitation source. Scanning electron microscopy (SEM) was carried out on a MEV JEOL JSM 6360LV Microscope. TGA measurements were performed under air on a TA Instruments 500 TGA 2050 using a heating rate of 10 °C min⁻¹ and platinum crucibles. Carbon, nitrogen and hydrogen amounts in insertion compounds were determined using a Perkin Elmer 2400 apparatus.

Results and discussion

³¹P MAS NMR Spectroscopy

Figure 1 presents the ³¹P MAS NMR spectra obtained for CeP70-4 and CeP90-4 samples. Both of them present only one resonance centered at –8.3 ppm. The chemical shift of the phosphate group is remarkably sensitive to its local environment. Hayashi *et al.* [15] performed ³¹P MAS NMR spectroscopic studies for CeP samples showing minimal formula Ce(HPO₄)₂·1.33H₂O and Ce(HPO₄)(PO₄)_{0.5}(OH)_{0.5}. The former showed a resonance at –7.2 ppm being attributed to P(OCe)₂(OH)₂. Otherwise, the latter showed resonances at –16.2, attributed to P(OCe)₃(OH), and –27.8 which was assigned as corresponding to P(OCe)₄. The substitution of a metallic atom coordinated to the phosphate group by a hydrogen atom leads to an variation near +10 ppm. Based on these observations, the resonance at –8.3 ppm may be associated to P(OCe)₂(OH)₂, indicating that CeP70-4 and CeP90-4 samples are composed exclusively by dihydrogenphosphate groups.

Thermal analysis

The t. g. curves of CeP70-4 and CeP90-4 samples are pictured in Figure 2. They present an abrupt weight loss of 14 and 16% for CeP70-4 and CeP90-4, respectively, initiated at the beginning of the heating and prolonged until near 700 °C. The solid obtained at 800 °C was characterized as CePO₄. Since ³¹P MAS NMR spectroscopic results indicate that CeP samples are formed by dihydrogenphosphate groups and taking account that the P/Ce molar ratio for CeP70-4 and CeP90-4 were quantified as 2, the general formula for CeP may be defined as CeO(H₂PO₄)₂·nH₂O. The crystallization water content (*n*) for each sample may be determined by the total weight loss at 800 °C. Since the formation of

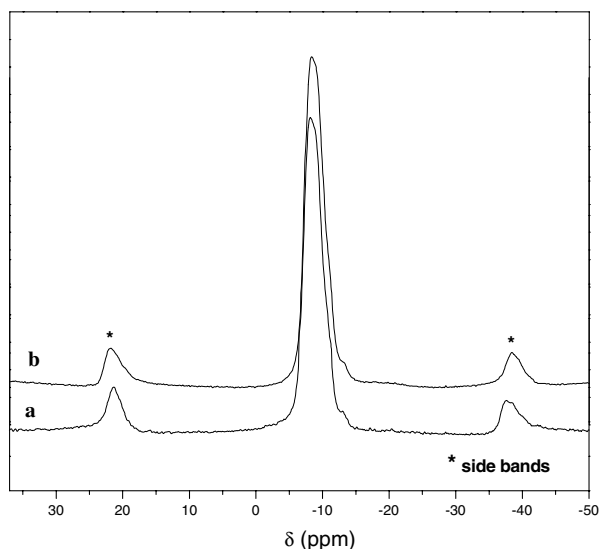


Figure 1. Solid-state ^{31}P MAS NMR spectra for the samples: (a) CeP-70/4, (b) CeP-90/4.

CePO_4 involves the dehydration of two mols of structural water, and 0.25 mol of O_2 per mol of CeP, n was quantified as 0.3 and 0.8 for CeP70-4 and CeP90-4, respectively.

The decomposition mechanism of CeP samples is unclear and will be studied later by performing ^{31}P MAS NMR measurements on thermally treated CeP samples.

The t. g. curves obtained for CeP70-4/ethylamine insertion compound are pictured in Figure 2. Also in this case, the solid obtained at 800 °C was characterized

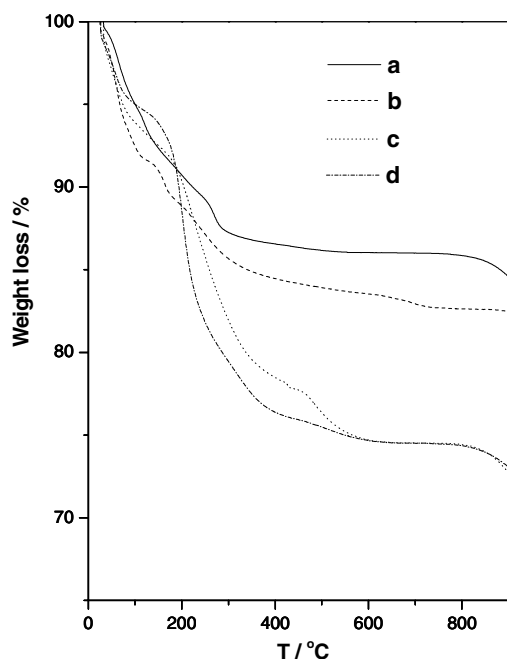


Figure 2. T. g. curves obtained for the samples (a) CeP70-4, (b) CeP90-4, (c) CeP70-4/ethylamine, and (d) CeP70-4/ ϵ -caprolactam.

as CePO_4 . The 25.5% weight loss observed is due to the elimination of two mols of structural water, 0.25 mol of O_2 , in addition to the amine content. Apparently, ethylamine insertion has expelled the water molecules from the interstitial region of CeP. Since the dehydration of structural water and O_2 evolving corresponds to a weight loss of 10.7%, the amine content may be determined as 14.8%, in good agreement with chemical analysis, which indicates an amine content near 15.6%. The molecular formula for this insertion compound may be determined as $\text{CeO}(\text{H}_2\text{PO}_4)_2(\text{CH}_3\text{CH}_2\text{NH}_2)_3$. This result shows that, despite CeP presents four acid sites, only three were exchanged. The probable reason for that is the steric hindrance between guest molecules. Very similar results were obtained for the CeP90-4/ethylamine compound.

The t. g. curve obtained for CeP70-4/ ϵ -caprolactam insertion compound is shown in Figure 2d. Also in this case, a 25.5% mass loss occurs before 700 °C and the solid obtained at 800 °C was also characterized as CePO_4 . Lactam insertion also eliminated crystallization water from CeP interstitial region, and the 14.8% weight loss may be attributed to the organic guest elimination, also in good agreement with chemical analysis, which points out a 15% lactam content. From this result, the molecular formula of the insertion compound is $\text{CeO}(\text{H}_2\text{PO}_4)_2(\text{C}_6\text{H}_{11}\text{NO})_{1.3}$. Not surprisingly, the bulky lactam molecule was inserted in smaller amount than the amine.

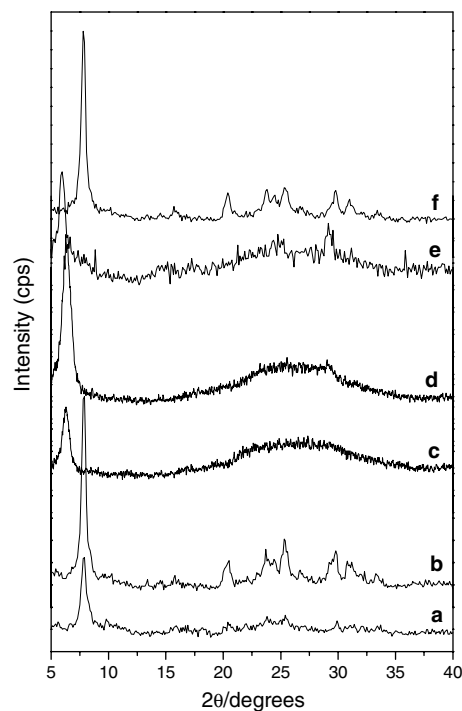


Figure 3. XRD patterns obtained for (a) CeP70-4, (b) CeP90-4, (c) CeP70-4/ethylamine, (d) CeP90-4/ethylamine, (e) CeP70-4/ ϵ -caprolactam, and (f) CeP90-4/ ϵ -caprolactam.

X-ray diffraction

The XRD patterns obtained for CeP sheets, before and after insertion procedures, are grouped in Figure 3. One can observe that for pure CeP samples the XRD patterns exhibit a characteristic intense peak at 7.9° (2θ), $d = 11.2 \text{ \AA}$, evidencing the porous nature of CeP structure. This peak and those located above 20° (2θ) are more intense and well defined for the CeP90-4 sample, suggesting that treatments involving higher temperature lead to more crystalline samples. The temperature-dependent process observed is consistent with an Ostwald ripening mechanism of crystallization.

The exposition of CeP sheets to a saturated ethylamine atmosphere led to several modifications in the XRD patterns. Firstly, one can observe a complete absence of well-defined reflections above 20° (2θ) for both CeP sheets, suggesting a significant loss of lattice ordering during the process. In addition, the above-mentioned peak located at 7.9° (2θ) becomes dislocated towards lower 2θ , pointing out an increase of the interplanar distance to 14.3 \AA for both CeP samples. This result clearly evidences the diffusion of the strong base towards the interstitial region of CeP.

A different behavior was found when we attempted to occlude a weak Lewis base, ϵ -caprolactam, in CeP samples. The literature reports several studies [17–25] in which ϵ -caprolactam is successfully intercalated in layered silicates. These processes are generally fast and proceed simply by stirring the silicate in an aqueous ϵ -caprolactam solution. However, such a procedure did not lead to an insertion compound when CeP was used in the place of a layered silicate. The situation was partially resolved by performing a more energetic procedure. The immersion of CeP sheets in fused ϵ -caprolactam led to different situations depending on the CeP sample. As one can observe in Figure 3, the CeP90-4 XRD pattern shows no significant alteration in the positions of its peaks when the more crystalline sheet (CeP90-4) was immersed in the fused ϵ -caprolactam, thus indicating that the weak base was not inserted. On the other hand, the same procedure displaces the peak initially located at 7.9° in the CeP70-4 XRD pattern towards lower 2θ values, revealing an increase of 3.9 \AA in the interplanar space.

The behavior shown by CeP towards insertion procedures could be associated to the energetic requirements for interplanar expansion. This energetic requirements must be supplied by the formation of new host–guest interactions, and it should be as intense as the attraction between adjacent planes, which in turn, is dependent on the plane size and, thus, on the crystallinity of the solid.

It is also evident that ethylamine insertion promotes the formation of strong host–guest interactions, which easily supply energetic requirements for interplanar expansion. In contrast, ϵ -caprolactam insertion does not lead to the same kind of interactions, but to weaker

ones, which, under the conditions used, makes insertion possible only with the less crystalline CeP sample.

Vibrational spectroscopy

Although CeP structure remains not elucidated, its behavior toward insertions procedures is typical for layered compounds, since the insertion of the guest performs an expansion of the interstitial space. For this reason, the success or failure of an insertion procedure involving CeP could be confirmed by means of XRD pattern results as presented above. However, they do not allow us to infer about the nature of the chemical bonds involved between host and guest species. FTIR spectroscopy is a useful technique for the characterization of insertion compounds involving amines. The formation of the alkyl-ammonium cation (R-NH_3^+) is easily identified in the spectrum by the appearance of a new $\delta(\text{H-N-H})$ resulting from the modification of hydrogen number and local symmetry of the amine groups, influencing their fundamental vibration modes. While $\delta(\text{H-N-H})$ is a degenerated mode for $-\text{NH}_2$ group, two angular deformation modes are expected for $-\text{NH}_3^+$ [26, 27].

As one can observe in Figure 2, the aqueous ethylamine solution spectrum shows the $\delta_d(\text{H-N-H})$ mode, at 1600 cm^{-1} , as a shoulder on the intense absorption band assigned to water. Protonated amines present their $\delta_{\text{assym}}(\text{H-N-H})$ mode from NH_3^+ group also at around

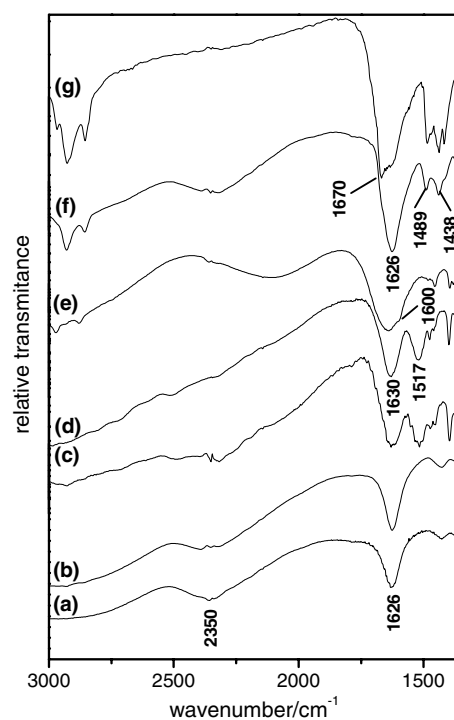


Figure 4. FTIR spectra obtained for the samples (a) CeP70-4, (b) CeP90-4, (c) CeP70-4/ethylamine, (d) CeP90-4/ethylamine, (e) ethylamine aqueous solution, (f) CeP70-4/ ϵ -caprolactam, and (g) pure ϵ -caprolactam.

1600 cm^{-1} , however, the symmetric mode generally occurs in the range from 1550 to 1500 cm^{-1} [28].

One can observe in Figure 4 that pure CeP sheets exhibit similar absorptions bands at 1626 and 2350 cm^{-1} , attributed, respectively, to occluded water molecules and to the $\nu(\text{PO}-\text{H})$ from acid phosphate groups, which give to CeP its Lewis base-exchanger character. It should be noted in Figure 4 that spectra obtained after ethylamine insertion procedure are not simply a superposition of those obtained from the individual components. The insertion compound spectra exhibit intense bands centered at 1630 and 1517 cm^{-1} . The former occurs in the same spectral region as expected for water or even for neutral amine deformation modes, thus not being conclusive on whether or not ethylamine molecules become protonated. However, no absorption has been observed for pure CeP or neutral ethylamine at the same spectral region as the latter, implying that undoubtedly it corresponds to the $\delta_{\text{sym}}(\text{H}-\text{N}-\text{H})$ mode, which in turn, characterizes the protonated state of the inserted ethylamine.

Agreeing with the conclusion above, Figure 4 also shows that the CeP band centered at 2350 cm^{-1} undergoes intensity losses. Since this band has been attributed to $\nu(\text{PO}-\text{H})$ mode, this phenomenon suggests a proton transfer, resulting from an acid-base reaction, which drives the insertion mechanism. Therefore, it seems to be clear that host-guest interactions between CeP and ethylamine have a predominant Coulomb-type component. Similar results were shown by procedures involving several examples of *n*-alkylamines, suggesting that the formation of strong host-guest bonds energetically favors the insertion. In contrast, weak bases impose critical difficulties to their insertion, as shown by the XRD pattern.

Figure 4 also presents the FTIR spectrum obtained for CeP70-4 after ϵ -caprolactam insertion procedure. The absorptions at 2930 and 2856 cm^{-1} associated to $\nu(\text{CH}_2)$, 1438 cm^{-1} assigned to $\delta(\text{CH}_2)$, 1626 and 1489 cm^{-1} attributed to amide I and amide II, correspond to guest modes. Comparing the position of these last two absorption bands with respect to where they are found in the pure ϵ -caprolactam spectrum, also shown in Figure 4, it is evident that insertion red-shifts the amide I mode.

According to Triggs and Valentini [29], ϵ -caprolactam amide I and amide II modes behave differently when ϵ -caprolactam takes part in hydrogen bonding in aqueous and other solutions. The amide I mode, which is essentially formed by $\nu(\text{C}=\text{O})$, becomes red-shifted since the carbonyl groups are involved in hydrogen bonds. Amide II mode arises from a combination between $\delta(\text{N}-\text{H})$ and $\nu(\text{C}-\text{N})$. Then, it should be perturbed as well. Since ϵ -caprolactam amide II is not significantly affected by hydrogen bonds, this mode is assumed to be formed essentially by the $\nu(\text{C}-\text{N})$ vibration [29].

Clearly, FTIR spectroscopic information points out that the host-guest interactions in CeP70-4/ ϵ -caprolactam system should occur via hydrogen bonds between

CeP70-4 acidic sites and ϵ -caprolactam groups ($\text{C}=\text{O}$ and $\text{N}-\text{H}$). If compared to the Coulombic forces, hydrogen bonds correspond to weak interactions. So, it is reasonable to realize that the formation of such interactions did not energetically favor the insertion procedure of ϵ -caprolactam, more drastic conditions being necessary as described earlier.

Raman spectroscopy was employed to investigate the spectral region from 100 up to 1200 cm^{-1} , where phosphate group vibration modes are expected. As one can observe in Figure 5, the CeP Raman spectra present three different sets of bands: two well-defined bands below 300 cm^{-1} associated with lattice modes; at least five bands found between 350 and 600 cm^{-1} , assigned to $\delta(\text{O}-\text{P}-\text{O})$ modes and, finally, five bands in the range from 900 to 1200 cm^{-1} that may be attributed to $\nu(\text{P}-\text{O})$ modes [30–32].

After ethylamine insertion, significant modifications were observed in the profiles of phosphate bands, which become wider, less well defined, and also occur in non-equivalent wavenumbers compared to pure CeP. Such results suggest that the CeP phosphate groups become strongly perturbed, which is consistent with their deprotonation promoted by an acid-base reaction with the amine.

Figure 5 also presents the Raman spectrum obtained after insertion of ϵ -caprolactam in CeP70-4. In this case, it is noted that the intercalation did not lead to any important modification in the phosphate bands profiles. Therefore, the chemical nature of phosphate groups has not changed after ϵ -caprolactam insertion, once more suggesting that CeP acid sites were not deprotonated,

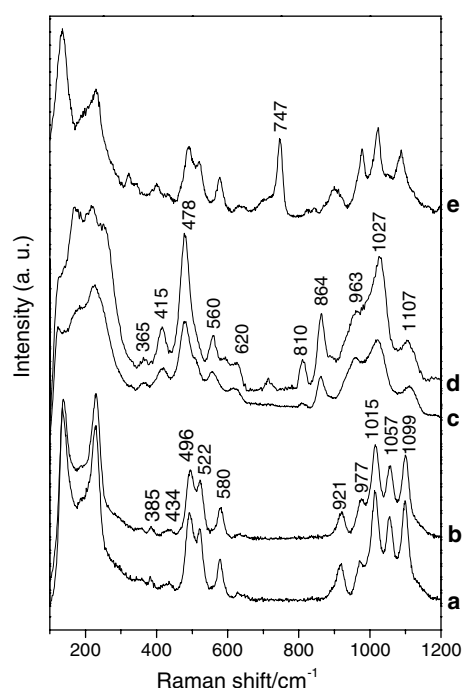


Figure 5. Raman spectra obtained for the samples (a) CeP70-4, (b) CeP90-4, (c) CeP70-4/ethylamine, (d) CeP90-4/ethylamine, and (e) CeP70-4/ ϵ -caprolactam.

which is consistent to the formation of hydrogen bond interactions.

Scanning electron microscopy

The scanning electron microscopy (SEM) images obtained for CeP70-4, CeP90-4 and for their insertion compounds are pictured in Figure 6. Both pure CeP samples show fiber morphology, however, the sample obtained using a higher reaction temperature presents a higher average fiber thickness.

Ethylamine insertion results in some modifications in the CeP morphology. Nevertheless, the fiber structure remains. Apparently, the fibers have swelled, leading to a more compact fiber organization. In contrast, CeP70-4 undergoes drastic changes in its morphological features during ϵ -caprolactam insertion. Figure 6e presents a SEM image (2000 \times) of a fractured region of the ϵ -caprolactam insertion compound. One can observe two distinct structures in the sample. Its surface (Figure 6f) is dominated by an irregular morphology. Apparently, fibers have been destroyed by the drastic insertion

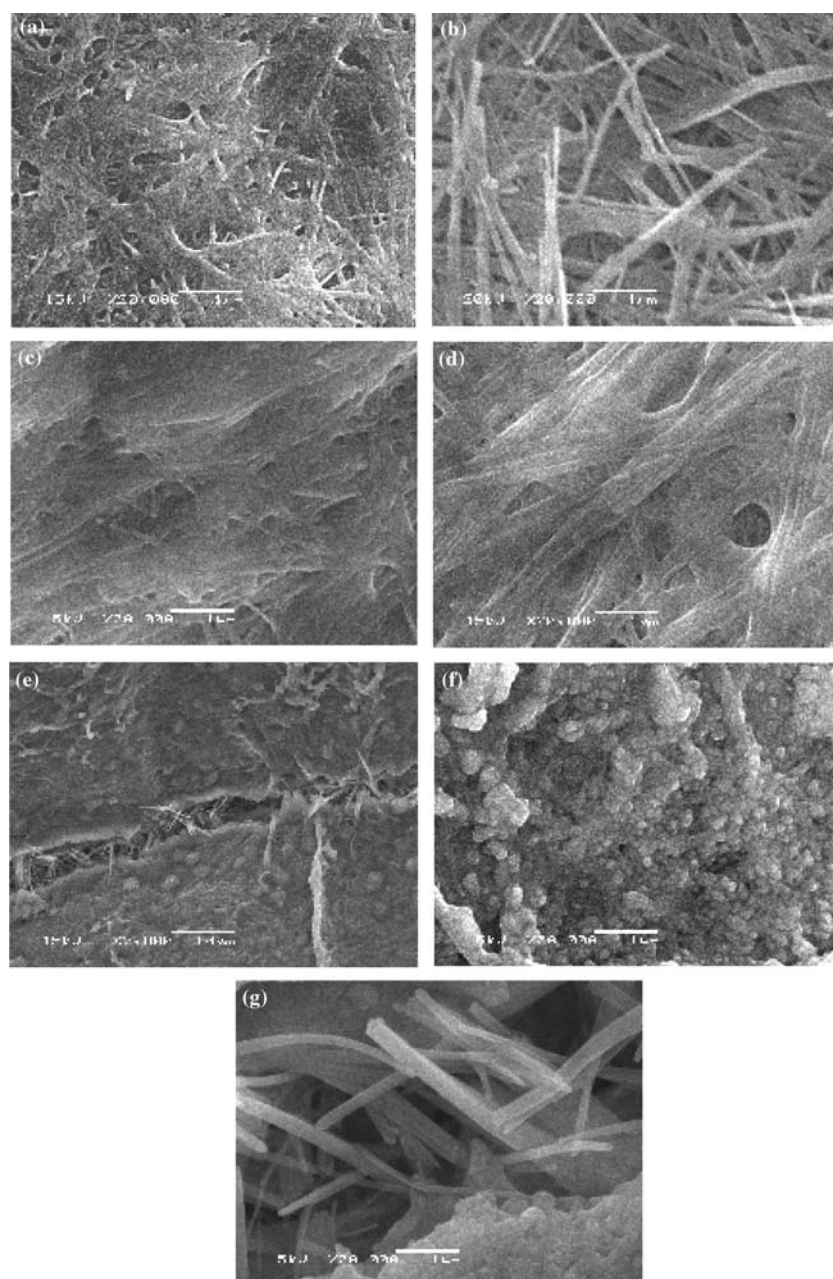


Figure 6. SEM images obtained for (a) CeP70-4, (b) CeP90-4, (c) CeP70-4/ethylamine, (d) CeP90-4/ethylamine, (e) fractured region of CeP70-4/ ϵ -caprolactam, (f) surface of CeP70-4/ ϵ -caprolactam at higher magnification, and (g) fracture of CeP70-4/ ϵ -caprolactam at higher magnification.

procedure. However, a look into the voids in the fractured surface of the sheet (Figure 6g) reveals that fibers remain intact in the interior of the sample. Notwithstanding, as mentioned earlier, XRD patterns show that the insertion reached even the innermost fraction of the sample since they were grounded before acquiring the XRD data.

Conclusions

The insertion behavior of CeP was studied by means of Lewis bases insertion procedures. It was shown that the formation of strong Coulombic type host–guest interactions energetically favors the formation of insertion compounds between CeP and strong Lewis bases, even considering that the process involves an entropy decrease since the amine, originally found in the gaseous state, is regularly deposited in CeP interstices.

In contrast, the insertion of ϵ -caprolactam was accomplished only with the less crystalline CeP sample, showing a relation between crystallinity and activation energy of insertion. By means of vibrational spectroscopy, host–guest interactions in these compounds were characterized as hydrogen bonds.

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