Journal of Thermal Analysis and Calorimetry, Vol. 87 (2007) 3, 775–778

SYNTHESIS AND THERMAL CHARACTERIZATION OF COPPER AND CALCIUM MIXED PHOSPHATES

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A series of compounds with composition of $Ca_{1-x}Cu_xHPO_4$, where x varied from 0.05 to 0.5 were synthesized by precipitation method. The compounds were characterized by elemental analysis, X-ray diffraction, infrared spectroscopy, scanning electron microscopy, and thermogravimetry. The chemical stabilities of solids were investigated at several pH. Elemental analysis of copper, calcium and phosphorus are in agreement with the proposed composition. The formation of lamellar phosphates was evidenced. The stability of the set of compounds was better for samples with high copper content.

Keywords: *calcium phosphate, copper phosphate, thermogravimetry*

Introduction

Nowadays, a large number of inorganic natural or synthesized materials have the incremented use in order to supply the demands of high modern nanotechnology. Among such classes of compounds those materials containing phosphates are characterized to have homogeneous properties with the advantage in forming many minerals and also biocompounds [1]. This versatility comes from the fact that the tetrahedral phosphate monomer units with great reactivity can condense as oligomers and polymers by forming open or close chains by inclosing a great variety of gel, crystalline or vitreous solids, in addition to microorganism constituents [2]. The anhydrous calcium phosphate can be obtained from the dehydration of brushita [3], hydrothermal synthesis [4] and obtaining through shelf-life of other phosphates at room temperature [5]. A prominence feature associated to phosphate is the enormous application in medicine and industry, which is focused to biological participation. Some phosphate derivates are potentially used as catalysts in heterogeneous catalysis. Depending on the nature of the cations linked to phosphate anion, they can exhibit acidic behaviour (Al^{3+}, B^{3+}), basic (alkaline and alkaline earth metals) or redox properties (transition cations) [6]. An interesting procedure for obtaining bifunctional catalysts based on the partial substitution of original cations such as Na^+, Li^+ and $(NH_4)^+$ by transition ions, e.g. copper in a phosphate with of Nasicon type or substitution of calcium by Co^{2+} and Ni^{2+} in tricalcium phosphate [6]. In this direction, a mixed phosphate composed of calcium and nickel with general formula $Ca_{3-x}Ni_x(PO_4)_2$ ($0\leq x\leq 0.275$) was used as catalyst for butene to butadienes [7] dehydrogenation. Phosphates containing calcium, sodium and copper in different compositions as $Ca_{10-5x}Cu_x(PO_4)_7$ ($0\leq x\leq 1$) and $Ca_{10-x/2}Na_xCu_{0.5}(PO_4)_7$ ($0\leq x\leq 1$) with the same structure of tricalcium phosphate β-$Ca_3(PO_4)_2$ was applied to catalyze the dehydrogenation of 2-butanol [8].

The aim of this investigation is the synthesis and thermal characterization of six calcium copper phosphates with general formula of $Ca_{1-x}Cu_x(HPO_4)$, where x varied from 0.05 to 0.5 by exploring also the stabilities of the new solids at several pH conditions.

Experimental

Materials

Chemicals

Ammonium phosphate $(NH_4)_2HPO_4$, calcium chloride $CaCl_2\cdot 2H_2O$ and copper nitrate hexahydrate $Cu(NO_3)_2\cdot 6H_2O$ were used without previous purification. Besides, deionized water was used in the preparations.

Synthesis of phosphates

This mixed phosphates were synthesized by precipitation method [9], mixing three aqueous solutions of

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1388–6150/$20.00

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$(NH_4)_2HPO_4$, $CaCl_2$ and $Cu(NO_3)_2$ with a 1.0 (Ca+Cu)/P ratio. Firstly, 100.0 cm^3 0.50 mol dm^{-3} of $(NH_4)_2HPO_4$ was heated at 373±10 K under reflux and stirring. To this hot solution both 0.10 mol dm^{-3} aqueous solutions of $CaCl_2$ and $Cu(NO_3)_2$ were slowly added and immediately a blue suspension was formed. The suspension was aged for 24 h at 373 K. The blue solid was separated by filtration, washed successively with water until a detection of negative chlorite test in the filtrated portion with silver solution. Finally the solid named CaP1 was dried at 573±10 K for 24 h. The total copper (x) and calcium (y) molar proportions were x=0.0475, y=0.0025; x=0.0450, y=0.0050; x=0.0400, y=0.0100; x=0.0350, y=0.0150; x=0.0300, y=0.0200 and x=0.0250, y=0.0250, resulting the materials named as CaCuPz (where z varied from 1 to 6).

Methods

The XRD patterns were obtained with nickel-filtered CuK_α radiation (λ=1.5406 Å and 2θ=1.5 to 70°) on a Shimadzu model XD3A diffractometer (40 kV/30 mA) with a speed of $1.67\cdot10^{-2\circ}$ s^{-1} at room temperature.

Calcium and copper elemental analyses in the synthesized compound were carried out through atomic absorption spectroscopy using GBC 808 AA apparatus. Phosphorus was quantified by spectrophotometric method using a Shimadzu MultiSpec-1501 spectrophotometer.

The morphology was studied through the micrographs analysis obtained by scanning electron microscopy. In order to examine these non-conducting materials, the samples were coated with a conducting layer of gold and carbon by sputter coating (Plasma Science Inc.). The images were obtained from the detection of the secondary electrons using Jeol JSTM-300 scanning electron microscope.

The thermogravimetric curves were obtained in an argon atmosphere on a TA Instruments 1090 B thermobalance at heating rate of 10 K min^{-1}, under a flow of 30 cm^3 s^{-1}, varying from room temperature to 1273 K, with an initial mass of approximately 10 mg of solid. The samples were not submitted to granulometric control.

Stability tests

The stability of solids was investigated by suspending a series of 100.0 mg samples of each copper calcium phosphate in 25.0 cm^3 of a buffer solution. The series of buffer solutions with well-established pH values of 4.2$C_8H_5KO_4$/HCl; 5.4HAc/NaAc; 7.0 and 8.7THAM/HCl, respectively were used. The suspensions were mechanically stirred for 24 h at 298±1 K and the solid was separated by centrifugation and dried at 393 K. The copper content was determined in duplicate for each samples of the supernatant by using GBC 808 AA atomic absorption instrument.

Results and discussion

Copper, calcium and phosphorus elemental analysis of the solids are in agreement with composition expected by formula $Ca_{1-x}Cu_x(HPO_4)$ as shown in Table 1.

The X-ray diffratograms of $Ca_{1-x}Cu_xHPO_4$ compounds are shown in Fig. 1 suggesting the formation of isostructural solids with the lamellar calcium phosphate [2]. The lamellar peak is corresponding to basal spacing of 998.0 pm. The value is not altered with the

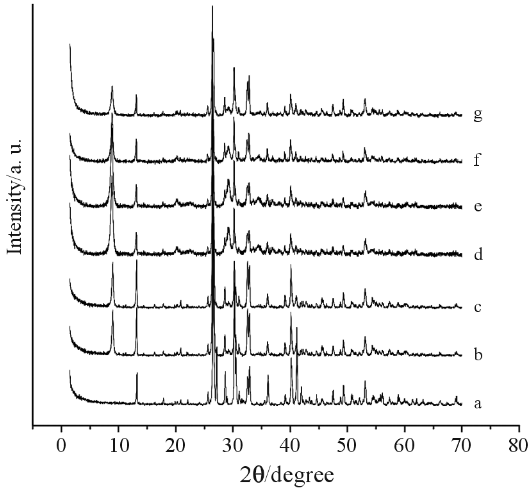

Fig. 1 XRD patterns of a – pure calcium phosphate and their copper doped form $Ca_{1-x}Cu_xHPO_4$ where x is b – 0.05; c – 0.10; d – 0.20; e – 0.30; f – 0.40 and g – 0.50

Table 1 Calculated (experimental) amount of calcium (Ca), copper (Cu) and phosphorus (P) for mixed phosphates (in mass%)

Phosphate	Ca/%	Cu/%	P/%
$CaHPO_4$	29.46 (29.30)	–	22.80 (22.40)
$Ca_{0.95}Cu_{0.05}HPO_4$	27.75 (27.60)	2.32 (2.29)	22.57 (22.40)
$Ca_{0.90}Cu_{0.10}HPO_4$	26.06 (25.90)	4.60 (4.50)	22.38 (22.25)
$Ca_{0.80}Cu_{0.20}HPO_4$	22.78 (22.70)	9.03 (8.95)	22.00 (21.70)
$Ca_{0.70}Cu_{0.30}HPO_4$	19.58 (19.30)	13.32 (13.21)	21.64 (21.30)
$Ca_{0.60}Cu_{0.40}HPO_4$	16.53 (16.42)	17.48 (17.39)	21.61 (21.31)
$Ca_{0.50}Cu_{0.50}HPO_4$	13.55 (13.49)	21.50 (21.25)	20.96 (20.56)

increasing of entrance of copper in the structure suggesting the maintaining of arrangement solid.

The scanning electron microscopy images confirmed the formation of single phases as it is shown in Fig. 2, demonstrating the presence of well-formed particles with regular shapes and sizes for both pure and mixed phosphates.

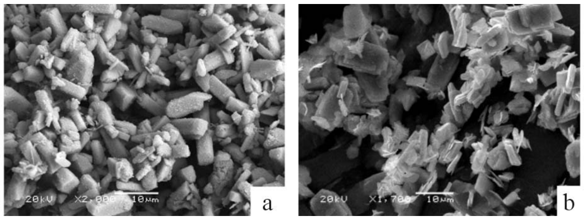

Fig. 2 Scanning electron microscope images of a – calcium phosphate $CaHPO_4$ and b – mixed phosphate $Ca_{0.95}Cu_{0.05}HPO_4$

The IR spectra of all copper phosphates are similar. The main absorption bands and their attributions in the 3700–3500 cm^{-1} range are due stretching vibration of O–H of water and structural OH; at 1620 cm^{-1} associated O–H bending of water; at 1087, 1030, 956 and 865 cm^{-1} related to stretching of P–O of the phosphate group [10, 11]. Other absorption bands are at 640 [$\nu_{P-O(H)}$ of HPO_4^{2-}]; 610 [δ_{O-H} of structural OH]; 560 [δ_{P-O} of PO_4^{3-}]; and 450 cm^{-1} [$\delta_{P-O(H)}$ of HPO_4^{2-}].

The chemical stability of calcium copper phosphates were performed under various pH conditions as indicated in Fig. 3. As it can be seen, all phosphate showed a degree of copper below 1.0% in acidic conditions. However, in basic condition the copper lixiviation is near to 3%, associated to the precipitation of their hidroxo complexes. The stability of phosphate in this pH range increased with copper concentration in the phosphate inorganic matrix. On the other hand, calcium phosphate is very stable in pH near to 7.0, while it can dissolve in pH below 4.0 and also above 8.0. As *t* was observed the thermodynamic stability of this series of the synthesized compounds is dependent on the participation of the copper entrance in the original inorganic backbone. From the viewpoint of bonding formation the alkaline earth metals has larger tendency in forming ionic compounds than the first series of metal transition. Thus, when the ionic radii is considered for calcium with 9.9 nm is replaced by copper with 6.8 nm in the inorganic structure [12] the last cation must adjusted in the crystalline arrangement with a certain degree of covalency in the doped phosphate with high stability at low pH. However, the copper cation entrance in the crystalline oxygen atom holes in the inorganic structure gives and additional stability due to the crystal field stabilization energy [12]. These effects can successfully contribute to the synthesis of these doped compounds.

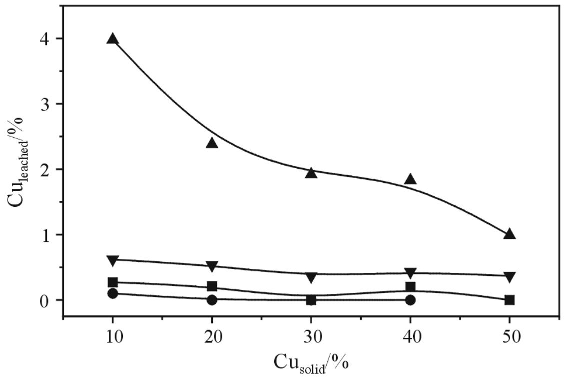

Fig. 3 Comparison of the lixiviated degree of copper from phosphates at pH ▼ – 4.2, ■ – 5.4, ● – 7.0 and ▲ – 8.7 and copper molar content in the solid

Thermogravimetry was used to characterize the thermal stabilities of solids. The total mass losses of $Ca_{1-x}Cu_xHPO_4$ were 7.3; 7.5; 8.1; 8.4; 9.3 and 9.5%, respectively for x=0.05; 0.5; 0.4; 0.3; 0.2 and 0.1 as summarized in Table 2 and Fig. 4. For calcium phosphate, three mass loss events were detected: the first one occurred due to loss of adsorbed water, the second one related to the formation of γ-$Ca_2P_2O_7$ by condensation of HPO_4^{2-} group accompanied by liberation of water, as suggested in the equation:

$$2CaHPO_4 \rightarrow \gamma\text{-}Ca_2P_2O_7 + H_2O$$

The third mass loss stage took place at 1030–1100 K where the γ-$Ca_2P_2O_7$ transformed to β-$Ca_2P_2O_7$ [13]. For doped phosphate, the decomposition below 450 K was associated to the evaporation of adsorbed water and between 660–845 K, the mass loss was related to the water elimination when HPO_4^{2-} transformed to γ-$P_2O_7^{4-}$:

$$2Ca_{1-x}Cu_xHPO_4 \xrightarrow{660-845\ K} \gamma\text{-}Ca_{2(1-x)}Cu_{2x}P_2O_7 + H_2O\uparrow$$

The last event above 1150 K was attributed to copper fusion with liberation of oxygen [14, 15], ob-

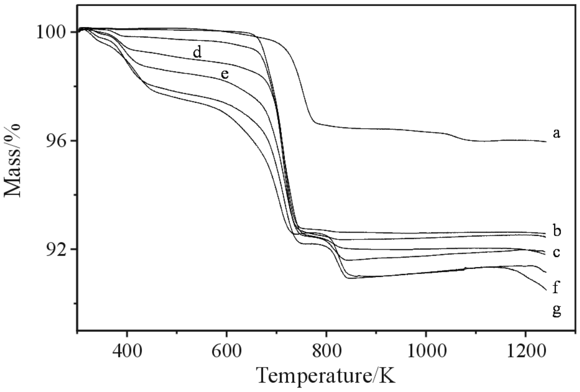

Fig. 4 TG curves of a – calcium phosphate and mixed phosphates containing copper in different molar percentages: b – 5, c – 50, d – 40, e – 30, f – 20 and g – 10%

Table 2 Mass losses from the TG curves of pure calcium and mixed phosphates

Phosphate	Δ*T*/K	Mass loss/%
$CaHPO_4$	300–350	0.2
	680–880	3.4
	1070–1120	0.3
$Ca_{0.95}Cu_{0.05}HPO_4$	637–747	7.3
$Ca_{0.90}Cu_{0.10}HPO_4$	312–450	2.1
	558–739	5.4
	788–861	1.4
$Ca_{0.80}Cu_{0.20}HPO_4$	1150–1273	0.6
	337–512	2.3
	587–742	5.4
	787–839	0.4
	1218–1273	0.3
$Ca_{0.70}Cu_{0.30}HPO_4$	367–428	1.2
	593–746	6.2
	793–846	1.0
$Ca_{0.60}Cu_{0.40}HPO_4$	347–403	0.7
	630–760	6.9
	761–836	0.5
$Ca_{0.50}Cu_{0.50}HPO_4$	357–404	0.2
	620–746	6.9
	747–819	0.4

served mainly for $Ca_{0.9}Cu_{0.1}HPO_4$ and $Ca_{0.8}Cu_{0.2}HPO_4$. The same behaviour was verified for other compounds resulting a mass loss lower than 0.2%. The highest loss of surface water for mixed phosphate suggested the hydrophilic behaviour is modified with the entrance of copper in the structure.

Conclusions

Mixed calcium copper phosphates were successfully synthesized by precipitation method using precursor reagents. All compounds were characterized and the stability assays were performed at different pH values. The structure of all doped phosphate was similar to lamellar calcium phosphate, which can be represented the series of compounds as $Ca_{1-x}Cu_xHPO_4$. Calcium and copper can be used in the superior to 4.0 and inferior to 8.7 pH range where the lixiviation process of these solids is minimized.

Acknowledgements

The authors are indebted to CAPES (E. C. S. F., O. G. S. and L. N. H. A.) and CNPq (M. G. F. and C. A.) for fellowships.

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DOI: 10.1007/s10973-006-7856-z