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PREPARATION AND THERMAL PROPERTIES OF A SERIES OF MIXED CALCIUM–COBALT PHOSPHATES

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Abstract

Mixed calcium-cobalt orthophosphates, of the general formula $Ca_{3-x}Co_x(PO_4)_2$ with $0\leq x\leq 1.1$, were prepared by coprecipitation. Reactions which occur during heating from room temperature to 850°C, of either tricalcium phosphate or mixed Ca–Co phosphates, were monitored by thermogravimetry and differential thermal analysis. The dried precipitates and the final products were characterised by X-ray diffraction and infrared spectroscopy.

Keywords: calcium orthophosphate, calcium-cobalt phosphate, thermal decomposition

Introduction

Phosphates are used in a variety of industrial processes because of their electrical, optical, magnetic and catalytic properties [1]. Their importance in industrial applications made them a subject of considerable interest for research on both practical and fundamental aspects.

The results herein form part of a wider study encompassing the preparation, characterisation and catalytic properties of mixed orthophosphates and orthoarseniates corresponding to the formula: $M_{3-x}M'_x(XO_4)_2$ where X = P, As; M = Ca, Sr, Ba and M'= Ni, Co, Zn, Cd.

In this paper we report on the preparation of pure mixed Ca–Co phosphates, hereafter called CCP, by coprecipitation.

Thermogravimetry (TG) and differential thermal analysis (DTA) were employed to assess the thermal decomposition course of the precipitates obtained.

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Additionally, the progress of the structural change was followed using X-ray diffraction (XRD) and infrared spectroscopy (IR) which permitted identification of the final products.

Experimental

Reagent grade chemicals and freshly boiled deionised water were used for the synthesis of the catalysts. $CaNO_3$, $CoCl_2$ and NH_4NO_3 were supplied by Merck while $(NH_4)_2HPO_4$ and NH_4OH (d =0.92) were supplied by Prolabo.

Chemical analyses were carried out on samples of the product calcined at 850°C after dissolution in hot 2 mol/l HCl [2]. The amount of phosphorus was determined by gravimetry in the form of quinoline phosphomolybdate. Ca was precipitated as Ca oxalate which was dissolved and titrated with $KMnO_4$. Co was determined by means of atomic absorption method on a Perkin Elmer 403 instrument. The products are characterised by the molar ratio R =Co/(Ca+Co).

TG and DTA studies were performed with Setaram D80 and Setaram MTB 10–8 units, respectively. Curves were recorded over a temperature range up to 900°C at a heating rate of 5 deg·min^{-1}.

The XRD equipment used consisted of a CGR THETA 60 X-ray generator and a Seeman-Bohlin focalisaton chamber (r =72 mm). The powdered samples, mixed with NaCl as an internal standard, were rotated whilst being exposed to CoK_α radiation.

IR absorption spectra were registered on a Perkin Elmer 575 spectrophotometer from thin discs containing approximately 2 mg of sample and 300 mg of spectroscopic KBr.

Results and discussion

The method used initially for the preparation of CCP was similar to that used for the preparation of Ca–Ni [3] and Ca–Cd [4] orthophosphates and also Ca–Ni orthoarseniates [5]. It consisted of slowly mixing diluted solutions of $(CaNO_3+CoCl_2)$ and $(NH_4)_2HPO_4$ at a constant pH maintained by addition of NH_4OH.

The product of composition R =8.3% was choosen to set up the preparation procedure.

The product obtained at a pH of 8 presented, after calcination at 850°C, an XRD pattern similar to that of β-tricalcium phosphate (TCP) [6, 7] with a little shift of lines due to the replacement of Ca^{2+} (r =0.99 Å) by Co^{2+} (r =0.72 Å) ions. However, its IR spectrum (Fig. 1) presented intense bands in the regions 1200, 950 and 750 cm^{-1} which can be attributed to undesired pyrophosphate ions [8–10]. To avoid this, the precipitation *pH* was increased. Samples were thus prepared at chosen *pH* values of 8.5, 9.0, 9.1, 9.5 and 10.0. All products obtained exhibited an XRD pattern similar to that of β–TCP with a little line shift. Their IR spectra (Fig. 1) showed that the intensity of the bands attributed to pyrophosphate ions decreased as the *pH* was increased, and disappeared at a *pH* of 9.5. However, already at *pH* 9.0, the preparation becomes difficult and requires large amounts of ammonia solution to maintain the *pH* fixed during precipitation. In addition, the second exothermic peak in the DTA curves (Fig. 2) of samples prepared at a $pH \geq 9.0$, which could not be explained, indicates that there might be another phase present as impurity below detectable limits of XRD. Therefore, this method was abandoned, although the amount of Co in these samples was satisfactory (Table 1).

Another method similar to that used for the preparation of precipitated TCP [11] and mixed Ca–Mg orthophosphate [12] was tested. The resulting product was pure as characterised by XRD, IR and DTA (Figs 1 and 2). Hence, this latter method was used for the preparation of a series of CCP.

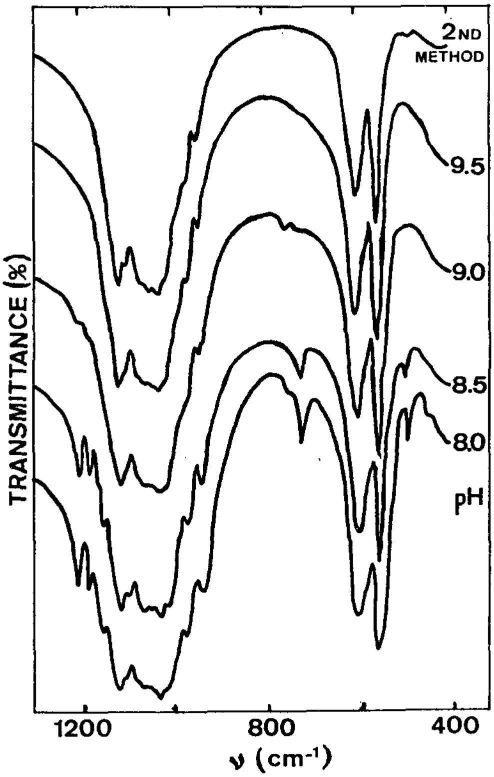

Fig. 1 IR spectra for mixed CCP prepared by different methods from solutions with $R = 8.3\%$, after calcination at 850°C

Table 1 Amount of cobalt in the solids prepared from solutions of composition R =8.3% (i.e. 4.68 wt% Co)

Product	*pH* 8	*pH* 8.5	*pH* 9	*pH* 9.1	*pH* 9.5	*pH* 10	2nd method
Co / wt%	4.53	4.43	4.46	4.63	4.46	4.55	4.45

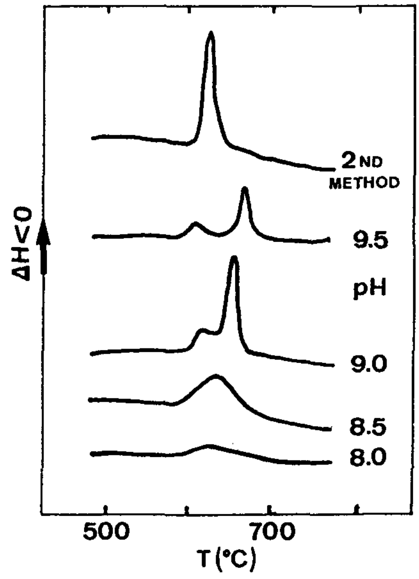

Fig. 2 DTA curves for oven dried CCP precipitates prepared by different methods from solutions with R =8.3%

The method consists of rapidly mixing, under vigorous stirring, two solutions, A and B, which have the following compositions:

solution A: 550 ml each of 0.30 mol/l $CaNO_3$, 0.30 mol/l $CoCl_2$ and 0.80 mol/l NH_4NO_3 solutions and 40 ml of concentrated NH_4OH;

solution B: 1300 ml of 0.15 mol/l $(NH_4)_2HPO_4$ solution and 40 ml of concentrated NH_4OH.

The blue-violet precipitates obtained were filtered and washed with ammoniacal water until all chloride was eliminated (test with $AgNO_3$). They were then dried in the oven at 70°C for 24 hours. After crushing and sieving, samples from the 40–60 μm fraction were activated by calcination at 850°C in a tubular furnace.

The chemical composition of various solids heated at 850°C (Table 2) shows that the overall stoichiometric ratio of cations to phosphorus, i.e. S=(Ca+Co)/P, is compatible with the value characteristic of orthophosphates, 1.50±0.02 when *R* was less than 10.7%.

Figure 3 shows the relationship between the molar ratios *R* in the final solids and the solutions used for their preparation. This ratio is always smaller in the solids and a linear relationship is found for samples with low Co concentration (less than 10.7%). This shows the difficulty presented by this method of preparation; as once the reactants are mixed, it is impossible to intervene to control the precipitation phenomenon and follow the formation of the products. Hence, it is always necessary to carry out chemical analyses to determine the right formula of the generated solids.

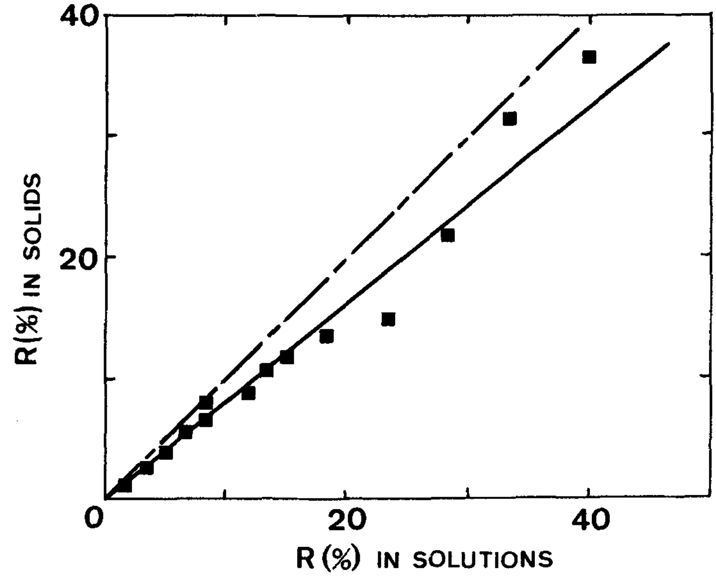

Fig. 3 Comparison between the Co content in the CCP catalysts and the solutions used for their preparation

The TG curves of CCP showed that the thermal decomposition of the precipitates takes place in two clearly separated stages. The first weight loss occurring between room temperature and 550°C is important and corresponds to dehydration of the precipitates. The second one appears above 600°C (Fig. 4); both its intensity and the temperature at which it occurs decrease when the amount of Co increases. It disappears when *R* reaches the value of 10.7%.

This observation can be related to the formation of precipitated TCP [13]. In this compound, constituted essentially of water, Ca^{2+} and PO_4^{3-} groups, the phosphate ions undergo, during drying, an internal hydrolysis which can be expressed by [11, 14]:

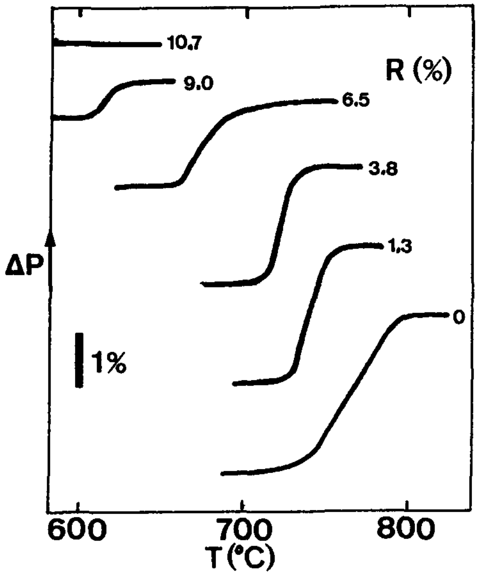

Fig. 4 TG curves for the CCP precipitates dried in the oven

Table 2 Chemical analysis of $Ca_{3-x}Co_x(PO_4)_2$ precipitates calcined at 850°C

In solution		In solids		
x	*R* / %	*C*/*P*	*R* / %	*x*
0	0	1.50	0	0
0.05	1.7	1.52	1.3	0.04
0.10	3.3	1.51	2.6	0.08
0.15	5.0	1.50	3.8	0.11
0.20	6.7	1.52	5.6	0.17
0.25	8.3	1.48	8.0	0.24
0.35	11.7	1.52	9.0	0.27
0.40	13.3	1.51	10.7	0.32
0.45	15.0	1.55	11.6	0.35
0.55	18.3	1.54	13.5	0.41
0.70	23.3	1.53	14.9	0.45
0.85	28.3	1.54	21.9	0.66
1.00	33.3	1.50	31.3	0.94
1.20	40.0	1.51	36.6	1.10

$$PO_4^{3-} + H_2O \rightarrow HPO_4^{2-} + OH^- \qquad (1)$$

This hydrolysis leads to a series of compounds with apatitic structure and of formulae:

$$Ca_9\square(HPO_4)_x(PO_4)_{6-x}(OH)_x\square_{2-x} \quad 0 \leq x \leq 1$$

The loss of water occurs in two distinct stages. The first one, between room temperature and 500°C, is due to the formation of pyrophosphate following the reaction:

$$HPO_4^{2-} \rightarrow 1/2P_2O_7^{4-} + 1/2H_2O \qquad (2)$$

The second one, between 740 and 780°C, accompanies the crystallisation of β-TCP:

$$P_2O_7^{4-} + 2OH^- \rightarrow 2PO_4^{3-} + H_2O \qquad (3)$$

It can be concluded that Co, which can give solvated complexes such as $[Co(H_2O)_6]^{2+}$, intervenes to slow down or even block the hydrolysis reaction thus stabilising the amorphous form. This explains the second mass loss and the phase transition temperature (apatitic- or amorphous-crystalline) decrease. Similar phenomena were observed in the case of Mn^{2+}, Mg^{2+} and Ni^{2+} ions [3, 12, 15, 16].

The DTA curves indicated the presence of a broad endothermic peak with its maximum at 130–150°C. Another peak was observed at higher temperatures. Starting from the TCP which exhibits an endothermic effect at 760°C which is due to water evolution during phase transition following reactions (2) and (3), when the amount of Co increases the intensity of the phenomenon, which becomes exothermic in the mixed CCP, increases and the temperature corresponding to its maximum decreases until the ratio of 9.0% is reached (Fig. 5). After this value, both the temperature and intensity of the phenomenon remain unchanged.

This confirms the observation made by TG in that the presence of Co^{2+} ions blocks the hydrolysis of PO_4^{3-} groups. The exothermic peak can then be attributed to the crystallisation of apatitic or amorphous CCP.

The IR spectra exhibited by the CCP catalysts calcined at 850°C (Fig. 6) correspond to that found for pure β-TCP [10, 17]. Typical for these spectra are the bands in the regions 1200–950 and 550–650 cm^{-1} which modes are relevant for PO_4^{3-} groups. The greater number of peaks in these spectra can be under-

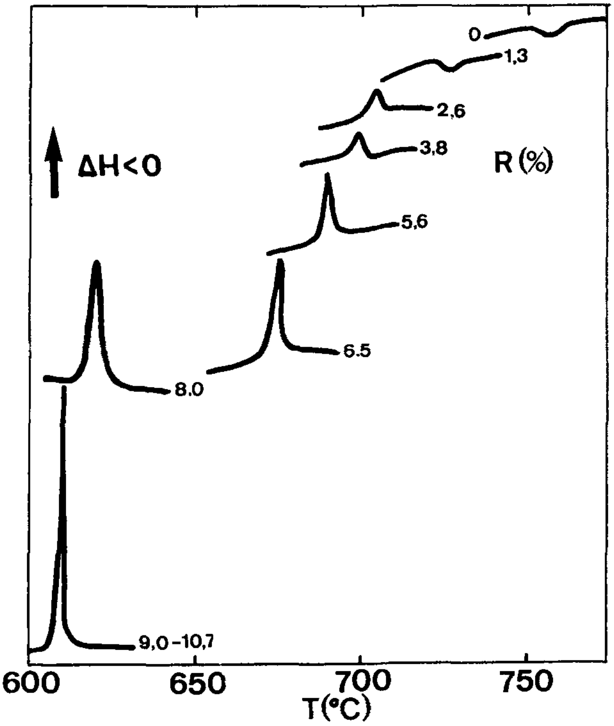

Fig. 5 DTA curves for the CCP precipitates dried in the oven

stood since the replacement of Ca^{2+} ions by Co^{2+} ions leads to distortions in the original structure of β-TCP.

It is worth noting that absorptions corresponding to $P_2O_7^{4-}$ ions were absent these spectra. However, the catalysts for which R >10.7% exhibited an additional IR band at 675 cm^{-1} which can be attributed to another phase which was identified by XRD to be of stanfeldite type.

XRD studies showed that the oven dried precipitates had a faint apatitic diffraction pattern for R equal to or less than 6.5%. Those with higher ratio were shown to be amorphous. This confirms the preceding observations in that the presence of Co favours the formation of initial amorphous gels.

After calcination, they were perfectly crystalline. Analysis of their diffraction patterns enabled their classification into two groups:

1. $R < 10.7\%$, samples were almost indistinguishable from each other and yielded d values that were in excellent agreement with those of β-TCP with a little line shift due to Ca replacement by Co.

2. $R \geq 10.7\%$, additional *d* spacings were observed inferring the presence of another crystalline component which was identified to be of stanfeldite type [18–20] (Table 3).

The cell parameters for all samples were refined with a least-squares computer program using the hexagonal setting of R3c. The change of the unit cell volume in relation with the amount of Co (Fig. 7) indicates that Vegard's law is obeyed. The solubility limit of Co in the β-TCP lattice was estimated at 10.3%. This value is in agreement with that determined by Nord [21].

Taking into account experimental errors, this value is compatible with the occupation of a certain type of sites in the structure of β-TCP. In fact, this structure contains five distinct Ca sites noted Ca (1) to Ca (5) by Dickens *et al.* [7]. These are reported in Table 4 with corresponding coordination number and percentage. Co^{2+} with its smaller radius tends to occupy preferentially octahedral sites. Site Ca (5) seems particularly favourable because of its shorter Ca–O bonds. This type of site has been observed to be occupied by Mg in whitlockite [22]. Meanwhile, a simultaneous occupation of neighbouring Ca (4) and Ca (5) sites can also be considered (9.52%) [23].

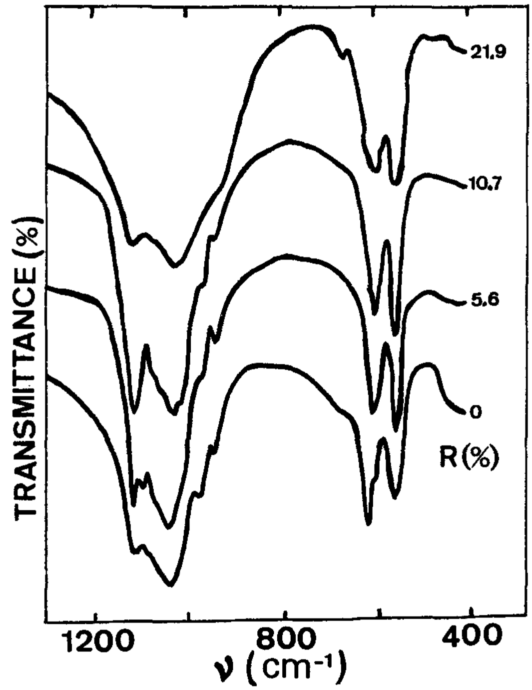

Fig. 6 IR spectra for the mixed CCP precipitates calcined at 850°C

Table 3 Comparison between *d* spacings ($I/I_0 \geq 20$) of stanfeldit and those of the phase obtained as a mixture with Co-substituted β–TCP in compounds with *R* >10.7%

Stanfeldite [20]		*R*= 21.9%	*R*= 31.3%	*R*= 36.6%
d / Å	I/I_0	*d* / Å	*d* / Å	*d* / Å
8.31	50			
6.01	50		6.009	5.996
5.00	30		5.028	5.013
3.84	60	3.853	3.854	3.846
3.75	80	3.749	3.750	3.744
3.25	30		3.448	3.265
3.04	30	3.057	3.057	3.056
2.817	100	2.814	2.813	2.811
2.734				
2.695	30			2.693
2.505	80	2.507	2.509	2.508

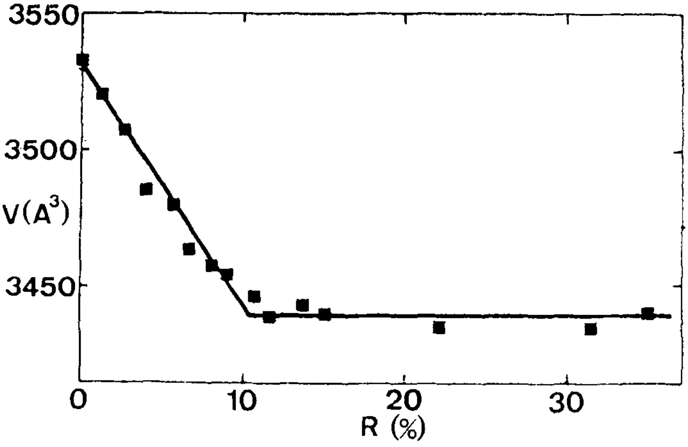

Fig. 7 Unit cell volume change with the amount of Co in the mixed CCP calcined at 850°C

Conclusion

Mixed CCP catalysts of a general formula $Ca_{3-x}Co_x(PO_4)_2$ ($0 \leq x \leq 1.1$) were prepared by coprecipitation.

Chemical analyses of the compounds obtained indicated that some Co is lost during coprecipitation.

Thermal analyses by TG and DTA of the precipitates showed that Co^{2+} ions intervene to block the hydrolysis of orthophosphate ions during drying, thus stabilising the amorphous form. These methods can be used to estimate the solubility limit of Co in the β-TCP structure (around 10%).

Table 4 Different types of sites in the rhombohedral structure of β-TCP (R3c) [7]

Site	Ca(1)	Ca(2)	Ca(3)	Ca(4)	Ca(5)
Coordination number	7	8	8	6	6
Percentage	28.57	4.76	9.52	4.76	9.52

IR and XRD methods showed that these phosphates were obtained by replacement of some Ca^{2+} ions by Co^{2+} ions in the β-TCP structure.

The solubility limit of Co in the β-TCP lattice was determined from the change in the cell volume with the amount of Co. It corresponds to 10.3%.

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Zusammenfassung — Mittels Kopräzipitation wurden gemischte Calcium-Cobalt-orthophosphate der allgemeinen Formel $Ca_{3-x}Co_x(PO_4)_2$ mit $0 \leq x \leq 1.1$ hergestellt. Die ablaufenden Prozesse beim Erhitzen von Tricalciumphosphat beziehungsweise gemischten Ca–Co-Phosphaten von Raumtemperatur bis auf 850°C wurden mittels TG und DTA untersucht. Die getrockneten Präzipitate und die Endprodukte wurden mittels Röntgendiffraktion und IR-Spektroskopie beschrieben.