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ACCURATE THERMOGRAVIMETRIC STUDIES OF HYDRATED CONDENSATED PHOSPHATES IMPLY CONTROLLED WATER VAPOUR PRESSURES

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ABSTRACT

The characterization of divariant dehydration and anion decondensation of hydrated condensed phosphates and the competition of these two phenomena imply thermogravimetric studies under controlled water vapour pressure and by mass step method.

INTRODUCTION

The stacking of finite anions of large size such as $P_3O_{10}^{5-}$ chain and $P_3O_9^{3-}$ ring leaves, in the crystal structure of some phosphates, cavities occupied by H_2O molecules which contribute little or nothing to the stability of the crystal framework and may be likened to zeolitic water.

Independent of these structural properties, the very nature of these condensed phosphate anions which are unstable in the presence of water suggests an irreversible decomposition of these compounds, the ultimate phase of any decondensation being the monophosphate.

Therefore, one must be prepared for the characterization of dehydration divariance and anion decomposition by thermogravimetric study of condensed phosphates.

TECHNIQUES AND METHODS

The thermogravimetric experiments have been carried out in a McBAIN microbalance, specifically designed to maintain a given vapour pressure (ref. 1). This thermobalance includes three parts (Fig. 1) : the thermoregulated jacket-laboratory tube system which contains the silica helix and the sample pan ; (ii) the "cold point" which establishes the controlled water vapour pressure from the $H_2O(\ell) \rightleftarrows H_2O(g)$ monovariant transformation (ref. 2) ; and (iii) the vacuum or air fillinq system of the apparatus.

The control of observed phases has been effected by X ray diffractometry and thin layer chromatography (TLC), a technique specially adapted to phosphate investigations (ref. 3).

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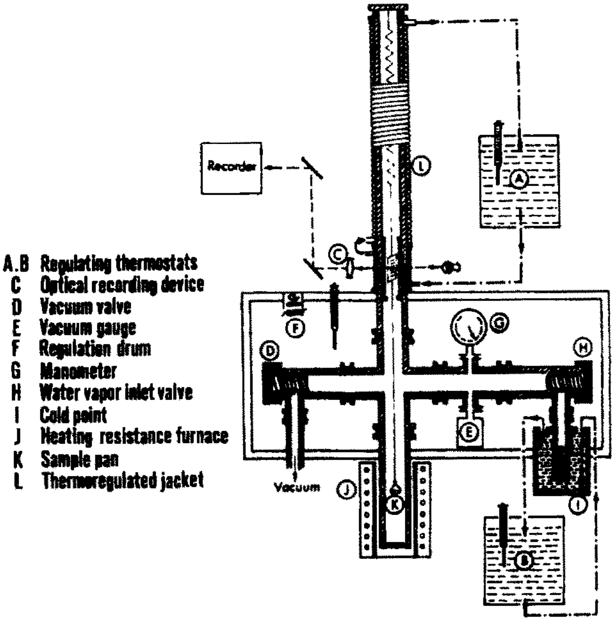

Fig. 1. Mc Bain-type thermobalance with automatic water vapour pressure regulator designated "cold point".

The thermogravimetric study of $H_2O(g)$-phosphate system has been realized from static experiments at constant temperature T and pressure p (constant nH_2O). From this operative procedure, it is possible to plot T, p and nH_2O,T diagrams from which the dehydration phenomenon will be distinguished from one of decondensation.

EXPERIMENTAL RESULTS

In order to prove the necessity of water vapour pressure control in hydrated condensed phosphates study, results on two tricyclophosphates which have zeolitic H_2O molecules are analysed here. It concerns lanthane tricyclophosphate LaP_3O_9 $3H_2O$, sodium-calcium tricyclophosphate $NaCaP_3O_9$ $3H_2O$. Like every condensed phosphate, these compounds are unstable (with atmospheric water vapour), their life varing from 6 to 18 months. Therefore, the stocks have been controlled and renewed.

Lanthane tricyclophosphate LaP_3O_9 $3H_2O$ (ref. 4).

The p, T diagram of system LaP_3O_9 $3H_2O$-$H_2O(g)$ shows three domains (Fig. 2): (i) a domain in which the exchanges between the solid H_2Os and $H_2O(g)$ result in

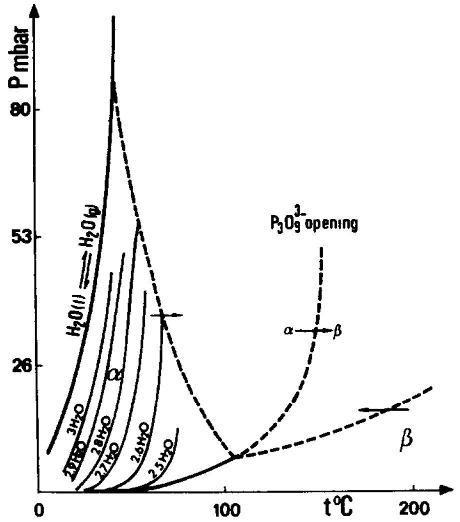

Fig. 2. P, T diagram of $LaP_3O_9\ 3H_2O-H_2O(g)$ system. ---- : irreversible,
—— : réversible.

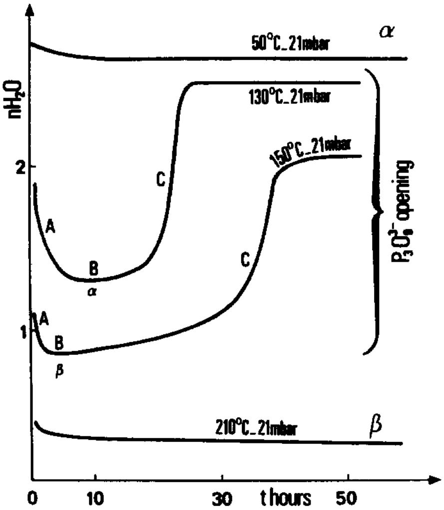

Fig. 3. Mass evolution of $LaP_3O_9\ 3H_2O$ with time

a divariant equilibrium, the trihydrated tricyclophosphate structure being conserved. This is the domain of the α phase stability, $LaP_3O_9\ xH_2O$ ($1 < x < 3$), characterized by its experimental network of isosters ; (ii) a domain of the β phase stability, $LaP_3O_9\ yH_2O$ ($0 \leqslant y \leqslant 1$), defined by the fact that the release of $2H_2O$ results in a slight contraction of the initial lattice along the c axis (ref. 5). Equilibrium between water vapour and the β phase is also divariant and for pressures below 8 mbar the α → β transformation is reversible ; and (iii) an instability domain of the tricyclophosphate resulting from the opennig of $P_3O_9^{3-}$ cycles and their irreversible decondensation according to :

$$P_3O_9^{3-} \xrightarrow{H_2O} PO_4^{3-} + (P_2O_5\ zH_2O)$$

The decondensation mechanism of $P_3O_9^{3-}$ cycle was followed by thermogravimetry. Indeed, the mass evolution curve versus time of tricyclophosphate sample put in the p and T conditions of the domain decondensation shows (Fig. 3) (i) stage A corresponding to the dehydration of the tricyclophosphate put in out-of-equilibrium conditions, with possibly the α → β transformation ; (ii) stage B in which a mass step occurs. According to the n value the coordinates p, T nH_2O of this step are along the extension of isosters plotted in the domains of the α phase ($n > 1$) and the β phase ($n \leqslant 1$). This mass step corresponds to the divariant equilibrium between $H_2O(g)$ and solid H_2Os ; and (iii) stage c in which the hydration of the phosphorous pentoxide occurs.

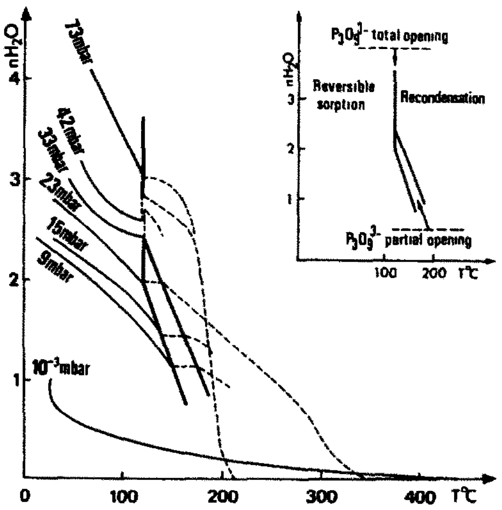

Fig. 4. n, T diagram of $NaCaP_3O_9$ $3H_2O$-$H_2O(g)$ system : ---- irréversible
—— réversible

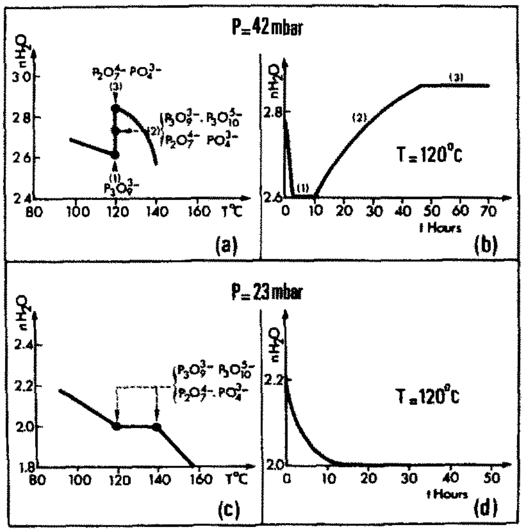

Fig. 5. $P_3O_9^{3-}$ ring opening process of $NaCaP_3O_9$ $3H_2O$: (a,b) p > 30 mbar,
(c,d) p < 30 mbar.

Sodium-calcium tricyclophosphate $NaCaP_3O_9$ $3H_2O$ (ref. 6).

The nH_2O, T diagram of system $NaCaP_3O_9$ $3H_2O(g)$ shows three domains (Fig.4): (i) a domain in which exchanges between the phosphate H_2Os and $H_2O(g)$ results in a divariant equilibrium, the tricyclophosphate structure being preserved. The isobar network characterizes it ; (ii) a domain in which a opening and a decondensation of the $P_3O_9^{3-}$ cycles occur with formation of an ill-defined mixture. If p $\geqslant$ 30 mbar this domain is restricted to a straight line. Decondensation, then, occurs at 120°C and it is total. Not being instantaneous, this decomposition was followed as a function of time (Fig. 5 a and b) and TLC analyses showed that it was the result of a hydrolysis similar to that observed in an aqueous medium according to :

$$(1)\quad P_3O_9^{3-} \xrightarrow{H_2O} P_3O_{10}^{5-} \xrightarrow{H_2O} PO_4^{3-} + P_2O_7^{4-}$$

If p $<$ 30 mbar, the hydrolysis is only partial and is characterized (Fig. 5 a and b) by the occurrence of a mass step showing a slowing down in the water release, resulting from a water consumption required by hydrolysis. In the absence of $H_2O(g)$ (10^{-3} mbar), this tricyclophosphate dehydrates entirely without the occurrence of decomposition. The resulting anhydrous differs from trihydrated tricyclophosphate, the anhydrous → hydrate transformation being reversible; and (iii) a domain in which the dehydration of mixture leads to recondensation of anions as $P_3O_9^{3-}$ cycles and formation of anhydrous. By heating, the anhydrous is irreversibly converted into polyphosphate $[NaCa(PO_3)_3]_\infty$.

RESULTS ANALYSIS

Dehydration study of these two tricyclophosphates shows that there is competition between dehydration and decondensation of cycles. The decondensation process is linked intimately to the water vapour effect (it is essential to work under controlled water vapour pressure), and like a slow phenomenon (it is essential to work by mass step).

Opening and decondensation process of the $P_3O_9^{3-}$ cycle, established from experiments before and from tetradecahydrate cadmium tricyclophosphate study (ref. 7 and 8) schematically accords to : (i) in the crystal, the H_2Os linked to cations are dissociated partially under the influence of time and temperature :

(2) $H_2O(\text{linked}) \rightarrow H^+ + OH^+$: self - protolysis as a function of time

(3) $\left.\begin{array}{l} H_2O(\text{linked}) \rightleftarrows H^+ + OH^- \\ \quad\text{low T} \qquad\qquad\quad \text{high T} \end{array}\right]$ equilibrium as a function of temperature at time given

(ii) protons are transferred on the external oxygens of cycle in order to create the entity $[3H^+ , PO_4^{3-}]$, tricyclophosphoric acid which is very unstable with water. The mobile H_2Os play the part of water and the decondensation-opening occurs according to (1) ; and (iii) in order to understand observed phenomena, it is necessary to consider a fourth reaction concerning divariant dehydration :

(4) $H_2O(\text{mobile}) \rightleftarrows H_2O(g)$

Several facts are explained then (i) tricyclophosphate instability results from reactions (2) and (1) ; (ii) water vapour pressure effect results in, with a pressure increase, non departure of mobile H_2Os [reaction (4) on the left] and the decondensation [reaction (1)] – and with a pressure decrease, the departure of mobile H_2Os [entirely or partially ; reaction (4) on the right] and the no (or partial) decondensation (Fig. 2 and 5) ; and (iii) temperature effect results in the decondensation by its increase [reaction (3) on the right]. Therefore, the water vapour effect on decondensation process is not direct, but it is bound by the displacement of equilibrium (4) with the pressure.

Finally, competition between dehydration and decondensation-opening (Fig.3 and 5) cannot be observed by thermogravimetric study with a temperature increase.

CONCLUSION

The example of the dehydration of hydrated condensed phosphates by thermogravimetry shows the necessity to have the control of the water vapour pressure, and to work with a mass step method. Only, the study by isobaric and isothermal mass step leads to characterize the competition between dehydration and anion decondensation (ref. 9).

REFERENCES

1 M.H. Simonot-Grange, Clays and clay minerals, 27, n° 6 (1979) 423-428.
2 A. Tiselius and S. Brohult, Phys. Chem. Abt. A 168 (1934) 248-256.
3 J. Aurenge, M. Degeorges, J. Normand, Bull. Soc. Chim. Fr. (1964) 508.
4 M.H. Simonot-Grange and D. Gobbled, J. Less. Com. Metals, 38 (1974) 167.
5 M. Bagieu-Beucher, I. Tordjman, A. Durif, Rev. Chim. Minérale, 8 (1971) 753.
6 M.H. Simonot-Grange and P. Jamet, Phosphorus Sulfur, 3 (1977) 197.
7 C. Dorémieux-Morin, Phosphorus Sulfur, 4 (1978) 39.
8 M.H. Simonot-Grange, J. of Solid State Chem. 46 (1983) 76-86.
9 M.H. Simonot-Grange, J. of Coll. and Interf. Sc. 70 (1979) 231-238.