Journal of Thermal Analysis, Vol. 37 (1991) 131-138

THERMAL DECOMPOSITION OF ORGANIC DERIVATIVES OF CRYSTALLINE ZIRCONIUM PHOSPHATE-PHOSPHITE

A. O. Rajeh and L. Szirtes

INSTITUTE OF ISOTOPES OF THE HUNGARIAN ACADEMY OF SCIENCES, H-1525
BUDAPEST, P.O.BOX 77, HUNGARY

(Received September 3, 1990)

Organic derivatives of crystalline zirconium phosphate-phosphite (ZrPP) are easily obtained by direct contact of the given organic solution with the crystalline material. The thermal decomposition of benzyl alcohol, benzylamine and some other aromatic compounds intercalated in ZrPP was examined. All examined samples lose their crystal water first at a relatively low temperature. The structural water is lost at a relatively higher temperature (in comparison with the crystalline α-zirconium phosphate derivatives).

The zirconium phosphate-phosphite (ZrPP) ion-exchanger was first investigated by Alberti and coworkers [1, 2], and we investigated the effects of modification of the preparation method and the mode of preparation of organic derivatives of this material [3, 4]. The double-layered ZrPP is a good intercalating agent for organic molecules containing COOH and/or NH_2 groups.

As part of this work, the thermal stability and thermal decomposition of organic derivatives were studied, and the results of these investigations are presented in this paper.

Experimental

Preparations

Preparations were carried out as follows: in each case, 100 ml of a saturated solution of the organic molecule added dropwise to 1.0 g of zirconium phosphate-phosphite (ZrPP). The ZrPP was equilibrated with this solution for five days at room temperature.

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

The precipitate formed was then separated, washed, air-dried and stored in a desiccator above phosphorus pentoxide, at room temperature (25±2°) until use.

For the experiments, the following organic materials were used: benzyl alcohol, benzylamine, *p*-nitrobenzoic acid, hippuric acid and phenylphosphonic acid. The organic derivatives were identified by analytical, X-ray powder diffraction and IR spectrophotometric methods under the conditions described earlier [4]. The thermal behaviour of the materials was investigated with a MOM-C derivatograph under the conditions described earlier [5].

Results and discussion

The results can be summarized as follows:

Benzyl alcohol intercalated zirconium phosphate-phosphite.

The curves in Fig. 1 show endothermic peaks with weight loss at 30°, 120°, 510° and 700°, and exothermic peaks without weight loss at 450° and 950°. The first two endothermic processes relate to the loss of the alcohol group and the crystalline water, and third to the loss of the benzyl ring, and the fourth to the loss of structural water. The two exothermic processes relate to the changes in the phosphite group and in the crystal structure of zirconium dioxide, respectively. The thermal decomposition of the material may be described as follows:

$$\mathrm{Zr[(HPO_4)(C_6H_6OPO_3)]\cdot 0.5H_2O} \xrightarrow[30^{\circ}\rightarrow 120^{\circ}]{\substack{-\mathrm{OH} \\ -0.5\mathrm{H_2O}}} \mathrm{Zr[(HPO_4)(C_6H_6OPO_3)]}$$

$$\xrightarrow[420^{\circ}]{} \mathrm{Zr[(HPO_4)(PO_3)]} \xrightarrow[510^{\circ}]{} \mathrm{ZrP_2O_7} \xrightarrow[700^{\circ}]{} \alpha\text{-}\mathrm{ZrO_2} \xrightarrow[950^{\circ}]{\substack{\text{cryst.} \\ \text{change}}} \beta\text{-}\mathrm{ZrO_2}$$

Benzylamine intercalated zirconium phosphate-phosphite. Figure 2 reveals endothermic peaks with weight loss at 40°, 135°, 510° and 700°, and exothermic ones without weight loss at 450° and 900°. The first two endothermic processes relate to the loss of the crystalline water and the amine, the third to the loss of the benzyl ring, and the fourth to the loss of structural water. The two exothermic peaks relate to the changes in the phosphite and in the crystal structure, respectively.

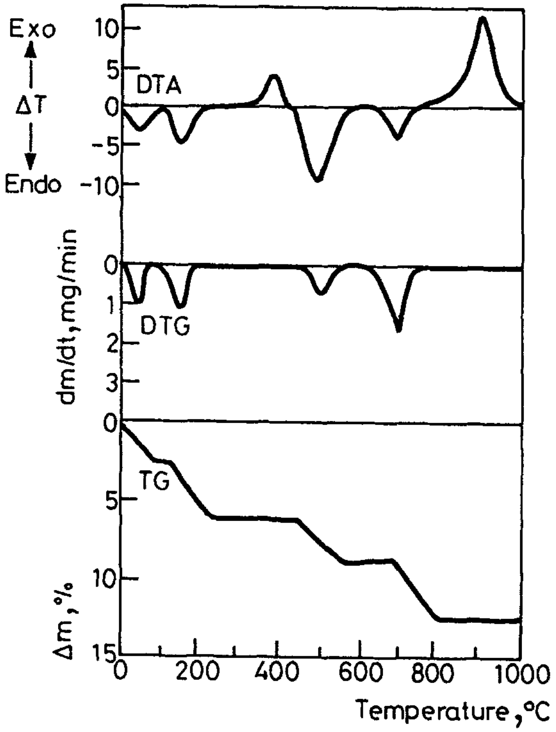

Fig. 1 Thermoanalytical curves of benzylalcohol intercalated zirconium phosphate-phosphite

The thermal decomposition of the material may be described as follows:

$$\mathrm{Zr[(HPO_4)(C_6H_8N.PO_3)]\cdot 0.5H_2O} \xrightarrow[40^\circ\rightarrow 135^\circ]{\substack{-0.5\mathrm{H_2O}\\ -0.5\mathrm{H_2O}}} \mathrm{Zr[(HPO_4)(C_6H_6PO_3)]} \xrightarrow[450^\circ]{}$$

$$\xrightarrow[450^\circ]{} \mathrm{Zr[(HPO_4)(HPO_3)]} \xrightarrow[510^\circ]{} \mathrm{ZrP_2O_7} \xrightarrow[700^\circ]{} \alpha\text{-}\mathrm{ZrO_2} \xrightarrow[900^\circ]{} \beta\text{-}\mathrm{ZrO_2}$$

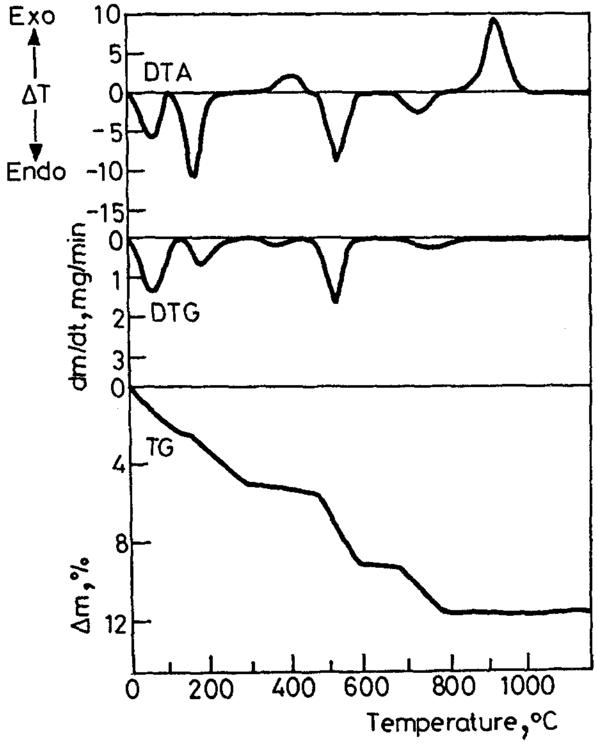

Fig. 2 Thermoanalytical curves of benzylamine intercalated zirconium phosphate-phosphite

Hippuric acid intercalated in zirconium phosphate-phosphite. Figure 3 shows endothermic peaks with weight loss at 60°, 200°, 405° and 700°, and exothermic processes without weight loss at 500° and 850°. The first two endothermic peaks relate to the loss of the crystalline water and the amine, the third to the liberation of the hippuric acid ring, and the fourth to the loss of the structural water. The two exothermic peaks relate to the changes in the phosphite group and in the crystal structure, respectively. The thermal decomposition of the material may be described as follows:

$$\mathrm{Zr[(HPO_4)(C_9H_9NO_3.PO_3)]\cdot 0.5H_2O} \xrightarrow[60^{\circ}]{0.5\mathrm{H_2O}}$$

$$\mathrm{Zr[(HPO_4)(C_9H_9NO_3.PO_3)]} \xrightarrow[200^{\circ}]{-\mathrm{NH_4OH}} \mathrm{Zr[HPO_4)(C_9H_5O_2PO_3)]}$$

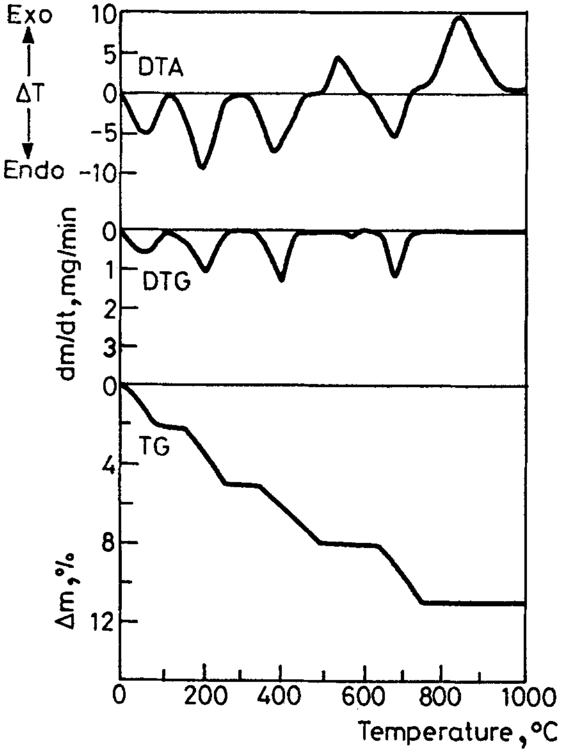

Fig. 3 Thermoanalytical curves of hippuric acid intercalated zirconium phosphate-phosphite

$$\xrightarrow[405^\circ]{\text{ringscission}} Zr[(HPO_4)(PO_3)] \xrightarrow[500^\circ]{-PO_3} Zr(HPO_4) \xrightarrow[700^\circ]{-H_2O} ZrP_2O_7 \longrightarrow$$

$$\longrightarrow \xrightarrow[850^\circ]{\text{crystalline change}} \alpha\text{-}ZrO_2 \xrightarrow[950^\circ]{} \beta\text{-}ZrO_2$$

p-Nitrobenzoic acid intercalated zirconium phosphate-phosphite. The curves in Fig. 4 demonstrate endothermic processes with weight loss at 40°, 130°, 240° and 460°, and exothermic processes without weight loss at 830° and 980°. The first two endothermic processes relate to the loss of the crystalline water and the amine, the third one to the loss of the benzoic ring, and the fourth to the loss of structural water. The exothermic processes relate to changes in the crystal structure. Calculations of the weight losses suggest that the thermal decomposition of the material may proceed as follows:

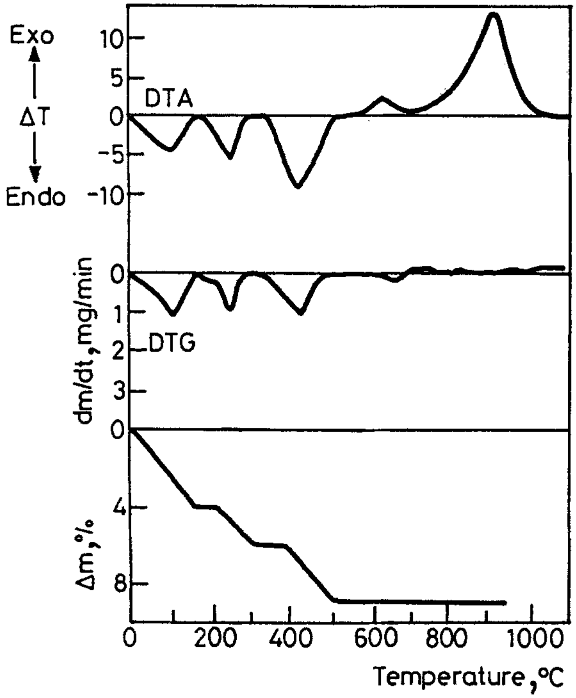

Fig. 4 Thermoanalytical curves of p-nitro benzoic acid intercalated zirconium phosphate-phosphite

$$\mathrm{Zr[(HPO_4)\cdot(C_7H_7NO_2\cdot PO_3)]\cdot 0.5H_2O} \xrightarrow[\text{till}\,130^\circ]{\substack{-\mathrm{CH_2\cdot N}\\ -0.5\mathrm{H_2O}}}$$

$$\mathrm{Zr[(HPO_4)(C_6H_6\cdot OPO_3)]} \xrightarrow[240^\circ]{\text{ring scission}} \mathrm{Zr(HPO_4)(PO_3)}$$

$$\xrightarrow[460^\circ]{-\text{structural water}} \mathrm{ZrP_2O_7} \xrightarrow[830^\circ]{} \mathrm{ZrO_2\cdot P_2O_5}$$

Phenylphosphonic acid intercalated zirconium phosphate-phosphite. The curves in Fig. 5 show endothermic peaks with weight loss at 60°, 510° and 700° and exothermic peaks without weight loss at 440° and 900°. The first two endothermic peaks relate to the loss of the crystalline water and the phenyl ring, and the third to the loss of structural water. The two exothermic peaks relate to the changes in the phosphite and in the crystal structure of zirconium dioxide.

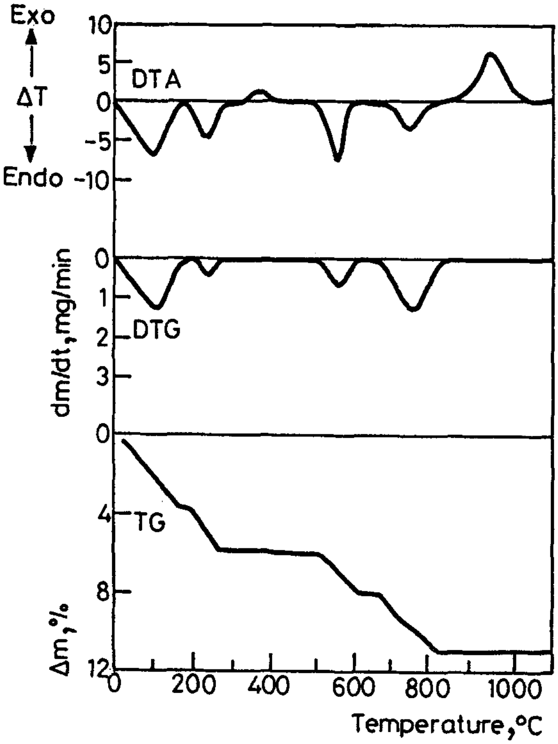

Fig. 5 Thermoanalytical curves of phenyl phosphonic acid intercalated zirconium phosphate-phosphite

The thermal decomposition of the material may be described as follows:

$$\mathrm{Zr[(HPO_4)(C_6H_7{\cdot}PO_3)]{\cdot}0.5H_2O} \xrightarrow[60^{\circ}]{0.5\mathrm{H_2O}} \mathrm{Zr[(HPO_4)(C_6H_7{\cdot}PO_3)]}$$

$$\xrightarrow[440^{\circ}]{} \mathrm{Zr(HPO_4)(PO_3)} \xrightarrow[510^{\circ}]{-\mathrm{H_2O}} \mathrm{ZrP_2O_7} \xrightarrow[\approx 700^{\circ}]{} \mathrm{ZrO_2{\cdot}P_2O_5};$$

$$\alpha\text{-}\mathrm{ZrO_2} \xrightarrow[900^{\circ}]{\text{crystalline change}} \beta\text{-}\mathrm{ZrO_2}$$

If data are compared with those on the organic derivatives of α-zirconium phosphate [6], the latter are seen to be less stable against temperature than the ZrPP organic derivatives (the steps of decomposition occur at higher temperature). For each investigated material, the crystalline water is lost at about 200°, generally in two nearly equal steps. This is followed by the loss or reordering of the organic molecules, and then loss of the structural water at about 700°. In comparison with the decomposition of phosphates of tetravalent metals, the decomposition of the $\mathrm{HPO_4^{2-}}$ groups in these cases occurs at temperatures higher by about 200 deg.

Further, the processes connected with the formation of pyrophosphates and the change in crystal form of the zirconium dioxide were found to be the same as known for pure metal phosphates [7].

The results discussed above can help towards a better knowledge of the crystal structures of these materials.

References

1 G. Alberti, U. Constantino, J. Környei and M. L. Luciani-Giovagnotti, Reactive Polymers, 4 (1985) 1.
2 G. Alberti, U. Constantino and G. Perego, J. Solid State Chem., 63 (1986) 455.
3 A. O. Rajeh, Theses for Ph. D. Budapest, 1990.
4 L. Szirtes and A. O. Rajeh , J Solid. State Chem., in press..
5 L. Szirtes, Z. Pokó, S. K. Shakshooki, M. Ahmed, A. Dehair and A. Benhamed, J. Thermal Anal., 35 (1989) 895.
6 A. O. Rajeh and L. Szirtes, J. Thermal Anal., to be published.
7 A. Clearfield ed., Inorganic Ion Exchange Materials CRC Press Boca Raton FL 1982. Chp. I.

Zusammenfassung — Organische Derivate von kristallinem Zirkoniumphosphatphosphit (ZrPP) werden durch direkten Kontakt der kristallinen Substanz mit der gegebenen organischen Lösung problemlos erhalten. Es wurde die thermische Zersetzung von in ZrPP eingelagertem Benzylalkohol, Benzylamin und einiger anderer aromatischer Verbindungen untersucht. Alle untersuchten Proben geben zuerst bei relativ niedrigen Temperaturen ihr Kristallwasser ab. Strukturelles Wasser wird (im Vergleich zu kristallinem α-Zirkoniumphosphat) bei relativ höheren Temperaturen abgegeben.