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THERMAL BEHAVIOUR OF COPPER-DIMETHYL-PHENANTHROLINE SPECIES IN α- AND γ-ZIRCONIUM PHOSPHATES

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Abstract

Two methods are described in order to obtain copper-2,9-dimethyl-1,10-phenanthroline (dmp) coordination compounds intercalated between the layers of α-$Zr(HPO_4)_2{\cdot}H_2O$ and γ-$Zr(H_2PO_4)(PO_4){\cdot}2H_2O$: the direct intercalation of Cu-dmp complex species or the formation 'in-situ' of coordination compounds. With the first exchanger both methods lead to similar products with X-ray diffraction patterns practically identical. They contain Cu(II-I)-dmp complex species that confer to the solids an initially green colour slowly turning to yellow with time or temperature when the reduction of Cu(II) to Cu(I) is complete. With γ-$ZrP(H_2PO_4)(PO_4){\cdot}2H_2O$, only the direct insertion is successful. TG/DTA experiments permit a better understanding of what is occurring in the materials during the copper reduction step, in correspondance of which, a strong endothermic peak and a gain in weight can be observed. They also show how the difference in the structure and chemical formula of the two exchangers affect the thermal behaviour of the two series of compounds.

Keywords: α- and γ-zirconiumphosphates, copper, dimethylphenanthroline, intercalation, thermal behaviour

Introduction

The layered inorganic ion-exchangers with a non rigid structure such as the acid phosphates of tetravalent metals (Zr, Ti, Sn), are able to intercalate coordination compounds either by directly inserting the pre-formed complexes or by favouring their formation 'in-situ' from an ion-exchanged transition metal ion (t.m.i.) and a ligand previously intercalated between the layers of the exchanger. In our wide investigation on the subject, we have used various polar

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molecules with ligand properties such as aminoacids, aminoalcohols, but specially aromatic diamines (2,2'-bipyridyl (bipy), 1,10-phenanthroline (phen) and 2,9-dimethyl-1,10-phenanthroline (dmp)), and the α- and γ-zirconium phosphate, $Zr(HPO_4)_2{\cdot}H_2O$ (α-ZrP) and $Zr(H_2PO_4)(PO_4){\cdot}2H_2O$ (γ-ZrP) respectively, and γ-titanium phosphate, $Ti(H_2PO_4)(PO_4){\cdot}2H_2O$ (γ-TiP) as the ion-exchangers of the class. A large numbers of coordination compounds have been intercalated in this way in the interlayer region of these exchangers [1].

Generally, the exchanged t.m.i. maintain their oxidation state either when they are subsequently coordinated 'in-situ' with the mentioned aromatic diamines pre-intercalated in the exchangers or when complex species are directly inserted as such, e.g. $[Cu(phen)_2]^{2+}$ [2], and $[Ru(phen)_3]^{2+}$ and $[Ru(bipy)_3]^{2+}$ [3] in α- and γ-ZrP. However, in the case of copper with dmp, the Cu^{2+} ions slowly may change their oxidation state, gradually transforming into a thermodinamically more stable +1 state, depending on the actual operating conditions. We have already had evidence of the gradual reduction of Cu^{2+} in α-ZrP when copper-dmp complexes are formed 'in-situ' [4]. The copper reduction does not occurs with γ-ZrP containing pre-intercalated dmp [5].

In this paper we report a systematic investigation on the redox behaviour of the phases of α-ZrP and γ-ZrP containing Cu-dmp species either inserted as such or formed 'in-situ' between the layers of the exchangers. We also show the thermal properties of the different copper materials and those of α-ZrP and γ-ZrP only containing dmp, for comparison.

Experimental

The α-ZrP- and γ-ZrP-copper-dmp materials were prepared either by inserting the preformed Cu-dmp complexes in the pre-swelled ethanolic form of the two exchangers (method 1), or by tempting to form 'in-situ' the Cu-dmp complexes by contacting Cu^{2+}-acetate solutions with the previously prepared α-ZrP-dmp or γ-ZrP-dmp intercalation compounds (method 2). In this latter case α-ZrP-$dmp_{0.48}$, γ-ZrP-$dmp_{0.28}$ and γ-ZrP-$dmp_{0.45}$ were used. They were prepared as detailed in the references [3] for the α-ZrP derivative and [5] for the γ-ZrP compounds.

Method 1

The Cu-dmp derivatives were obtained by contacting the pre-swelled ethanolic forms of α-ZrP (α-ZrPEtOH) [6], having an interlayer distance (the d_{002} reflection) of 14.24 Å) and γ-ZrP (γ-ZrPEtOH [7], d_{002} = 16.41 Å) with a solution containing bis-neocuproine copper(II) complex species prepared according to Yamamoto *et al.* [8]. The solution was stored at 4°C to avoid any reduction to Cu(I). The solid/solution batch ratios were generally such that 1 mole of ethanolic form of α-ZrP or γ-ZrP was contacted with the volume of bis-neocuproine-copper solution just containing 1 mole of complex species. The batch experiments were performed at 4 and 45°C for 7 days. The solids were then filtered off, washed with distilled water and immediately submitted to X-ray diffraction. This operation was repeated for the materials dried in air at r.t.

Method 2

α-ZrPdmp$_{0.48}$, γ-ZrPdmp$_{0.28}$ and γ-ZrPdmp$_{0.45}$ were contacted with a 5 mmol·dm^{-3} Cu(II) acetate solution, in a solid/solution batch ratio such that the moles of Cu(II) in the contact solution were equal to those of diamine intercalated in the solid, i.e. $[Cu^{2+}]:[\overline{dmp}] = 1$ (a bar over dmp signifies its presence in the solid state). In some cases, higher $[Cu^{2+}]:[\overline{dmp}]$ molar ratios were employed in order to observe the effects of a greater copper content inserted in the solids. Contact times, temperatures, filtrations, X-ray diffraction, etc., were those of method 1.

The X-ray patterns of all of the materials obtained with both the methods show that the solid maintain the layered structure and possess a good degree of crystallinity. The α-ZrP-Cu-dmp compounds have an interlayer distance of 14.60 Å, whatever is the preparation method. For the γ-ZrP derivatives the materials prepared with method 1 have an interlayer spacing of 17.7 Å, while those prepared with method 2 maintain that of the two precursors γ-ZrPdmp$_{0.28}$ and γ-ZrPdmp$_{0.45}$, which is 17.7 and 19.4 Å respectively.

Physical measurements and chemical analyses

The thermal curves were recorded on a simultaneous TG/DTA Stanton Redcroft 1500 thermoanalyzer, Pt crucibles, heating rate 8 deg·min^{-1}, ignition up to 1200°C to constant weight in an air flow.

X-ray powder diffraction was used to follow phase changes undergone by the materials (especially monitoring the d_{002} reflection and its harmonics and have confirmation of the maintenance of the layered structure of the treated materials) with a Philips diffractometer. Ni-filtered CuK$_\alpha$ radiation was used, and measurements of 2Θ are believed to be accurate to 0.05°.

Copper uptake was found following the concentration changes in the supernatants by atomic absorption spectrometry with a Varian Techtron model 1100 D instrument. Water and dmp contents of solids were determined from the TG curves.

Results and discussion

With α-ZrP the two different preparation methods lead to the obtainment of materials with a very near chemical composition and identical X-ray diffraction patterns. With method 1 a solid phase with a typical composition α-ZrP[Cu(II-I)-dmp]$_{0.28}$·2.5H$_2$O is obtained, which, initially green, slowly changes towards a yellow colour, that of pure Cu(I)-dmp complex species [9]. Thus the reduction of Cu(II) occurs with time, but it is also hastened by the increasing of the temperature.

With method 2, where Cu(II) acetate solutions are contacted with α-ZrPdmp$_{0.48}$, the copper ions rapidly exchange with the protons present in the interlayer region of the intercalation compound and then coordinate 'in-situ' to dmp which is, however, partially eluted from the solid until an almost 1:1 Cu-dmp complex species is formed. A phase of composition α-ZrP[Cu(II-I)-dmp]$_{0.3}$·2H$_2$O is obtained, that is initially greenish, then changes to yellow after a few days, thus confirming that +1 is the stable oxidation of copper when this t.m.i. is coordinated to dmp [10].

In Fig. 1 the simultaneous TG/DTA curves of freshly prepared, green α-ZrP[Cu-dmp]$_{0.3}$·2H$_2$O (method 2) compound are reported. Between 140–160°C an unusual strong endothermic peak is found in concomitance with a slight in-

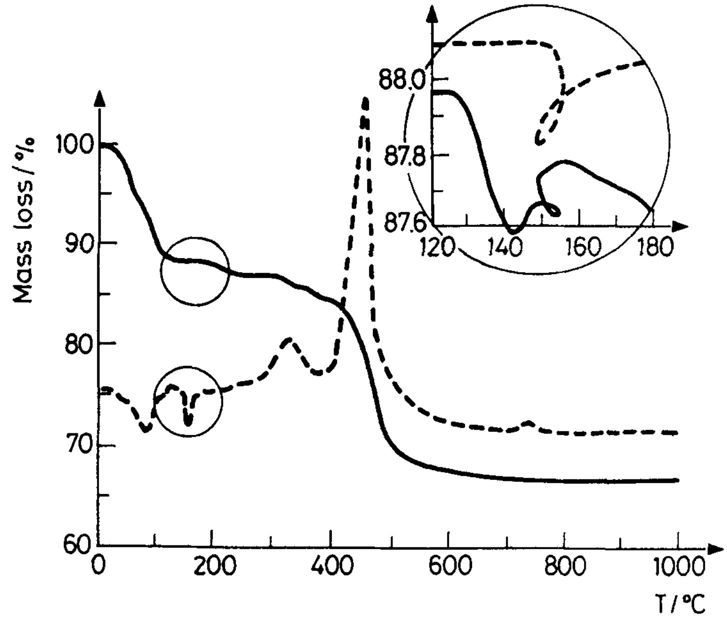

Fig. 1 TG and DTA curves of α-ZrP[Cu-dmp]$_{0.3}$·2H$_2$O

crease of weight (ca. 0.2%), as shown in the big circle of Fig. 1 which refers to the range of temperatures 120–180°C and obtained directly from the apparatus by highly enlarging the TG and DTA curves. This effect is always presented by the freshly prepared green materials, i.e. also from those obtained with method 1, while it is absent when the samples become definitely yellow. We explain this phenomenon as the consequence of the rapid increase of the temperature in the thermoanalyzer. When 130°C are reached, the Cu(II) present in the solid, linked to the neocuproine, undergoes a sudden reduction to Cu(I) and, in order to balance the negative charge now established in the interlayer region, a simultaneous assumption of protons become necessary. The overall reaction could be:

$$\alpha\text{-ZrP[Cu(II-I)-dmp]}_{0.3} + 0.15H_2O \rightarrow \alpha\text{-ZrP[H(I)Cu(I)-dmp]}_{0.3} + 0.075O_2.$$

No weight increment is observed in the same temperature range when Cu(I)-dmp is already present between the layers of the exchanger, i.e. when the material is yellow. This can be observed in Fig. 2 where are shown the TG and DTA curves of the yellow α-ZrP[Cu-dmp]$_{0.3}\cdot 2H_2O$ material, obtained from the just discussed green compound after a few days in air at r.t.: in the range of 130–150°C the endothermic peak in the DTA curve and the weight increment in the TG are no longer present. Furthermore, the shape of the thermal curves are now completely different. In Fig. 2 are also given the TG and DTA curves of α-ZrPdmp$_{0.48}$ for comparison.

When γ-ZrP is used as host phase, methods 1 or 2 give materials which behave very differently. With method 2, where γ-ZrPdmp$_{0.28}$ and γ-ZrPdmp$_{0.48}$ are employed, only pale blue products are obtained from both the starting intercalation compounds and, from their reflectance spectra [5] it is possible to assess that copper, which maintains its +2 oxidation state, does not coordinate to dmp but lies in an octahedral oxygen environment (O6). From the γ-ZrPdmp$_{0.45}$ host phase a small dmp elution takes place in concomitance with Cu^{2+} uptake and typical phases of composition γ-ZrPCu(II)$_{0.21}$dmp$_{0.45}\cdot 2.3H_2O$ or γ-ZrPCu(II)$_{0.31}$dmp$_{0.41}\cdot 1.3H_2O$ have been obtained depending on the amount of copper ions in the solid (the more Cu^{2+} ions enter the host, the higher the dmp elution). On the contrary dmp is not eluted from γ-ZrPdmp$_{0.28}$, even when molar ratios $[Cu^{2+}]:[\overline{dmp}] > 1$ (see experimental section) are considered and amounts of copper larger than 0.28 moles of Cu^{2+}/mole of material are exchanged. Pale blue phases of composition γ-ZrPCu(II)$_{0.20}$dmp$_{0.28}\cdot 2H_2O$ or γ-ZrPCu(II)$_{0.31}$dmp$_{0.28}\cdot 1.5H_2O$ have been obtained.

In Fig. 3 are reported the TG and DTA curves of γ-ZrPCu(II)$_{0.31}$dmp$_{0.28}\cdot 2H_2O$ and those of γ-ZrPdmp$_{0.28}$ for comparison. The elimination of the ligand from the copper containing material starts at ca. 300°C, i.e. at about one hun-

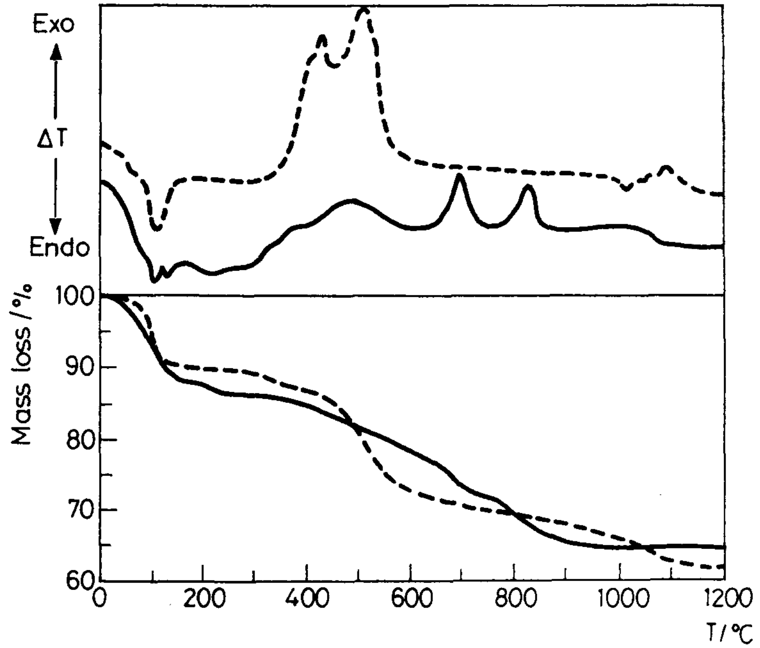

Fig. 2 TG and DTA curves of α-ZrP[Cu-dmp]$_{0.3}\cdot$2H$_2$O (yellow material) and α-ZrPdmp$_{0.48}$ (dotted lines)

dred degrees lower than for pure γ-ZrPdmp$_{0.28}$, and seems, in a certain way, assisted by the presence of the copper ions, since the process goes practically to completion at 700–800°C, instead of 1100–1200°C when copper is absent.

The different thermal behaviour of the α-ZrP and γ-ZrP materials only containing dmp can be easily noted in Fig. 4, where the TG and DTA curves of the two respective derivatives containing almost the same amount of ligand are reported. The TG curve of α-ZrPdmp$_{0.48}$ shows that dmp begins to be eliminated at ca. 250°C, while for γ-ZrPdmp$_{0.45}$ the process begins at about 380°C (same behaviour as that of γ-ZrPdmp$_{0.28}$ in Fig. 3). This means that the interaction (a protonation process [11]) between the nitrogen atoms of dmp and the acid phosphate groups present in the interlayer region of the host are much stronger in γ-ZrP than in α-ZrP. This is probably connected with the structure of γ-ZrP where PO$_2$(OH)$_2$ groups alternate with PO$_4$ groups [12]. The higher thermal stability of dmp in γ-ZrP is indicative of a greater ligand-matrix interaction and, consequently, a lesser tendency either to break this bond or to give rise to coordination compounds with copper ions. In fact, after the H$^+$/Cu^{2+} ion exchange process, the copper taken up does not coordinate with dmp, the ligand is not eluted from γ-ZrPdmp$_{0.28}$ and only a little from γ-ZrPdmp$_{0.45}$ when high loadings of Cu^{2+} ions are achieved in the solid (compare with the behaviour of α-

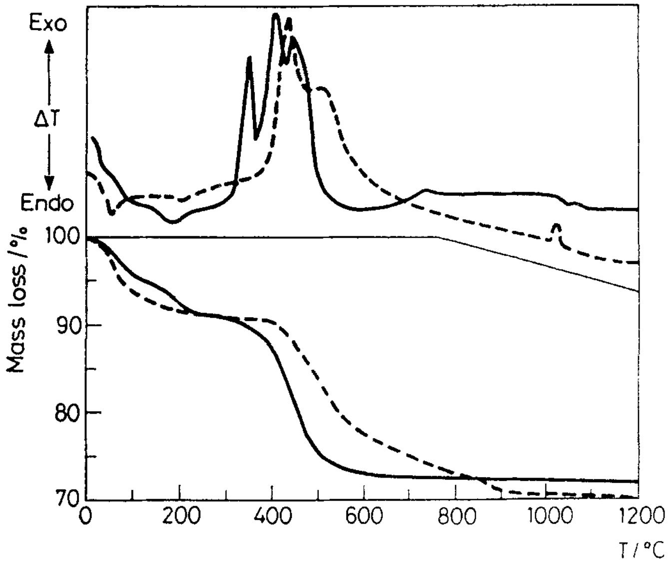

Fig. 3 TG and DTA curves of γ-ZrPCu(II)$_{0.31}$dmp$_{0.35}$·2H$_2$O and γ-ZrPdmp$_{0.28}$ (dotted lines)

ZrPdmp$_{0.48}$). In the case of α-ZrP the weaker interaction of the diamine with the uniformly distributed PO$_3$-OH groups of the interlayer region permits to dmp to move more freely and form Cu(II-I)-dmp coordination compounds.

The intercalation of Cu-dmp complex species in γ-ZrP is obtained by using method 1, that is by contacting the γ-ZrPEtOH phase with Cu-dmp complex containing solutions. Green materials are initially obtained (turning to yellow with time), with Cu/dmp molar ratios around 1. Also in this case, the green materials give TG and DTA curves that account for an endothermic effect associated with a small weight increment in the range of temperatures of 140–160°C, as for the corresponding α-ZrP compounds.

In Fig. 5 the thermal curves of yellow materials obtained with method 1 from α-ZrP and γ-ZrP are reported: in both α-ZrP[Cu(I)-dmp]$_{0.35}$ and γ-ZrP[Cu(I)-dmp]$_{0.25}$, the elimination of the ligand starts at about 300°C and is complete around 750°C, thus confirming the catalytic effect of copper in the combustion of dmp also for the γ-ZrP derivatives.

Conclusions

The compounds here investigated can be considered rather complicated systems. Several factors can affect their chemical composition, the copper oxidation state and its possibility of forming complex species with neocuproine.

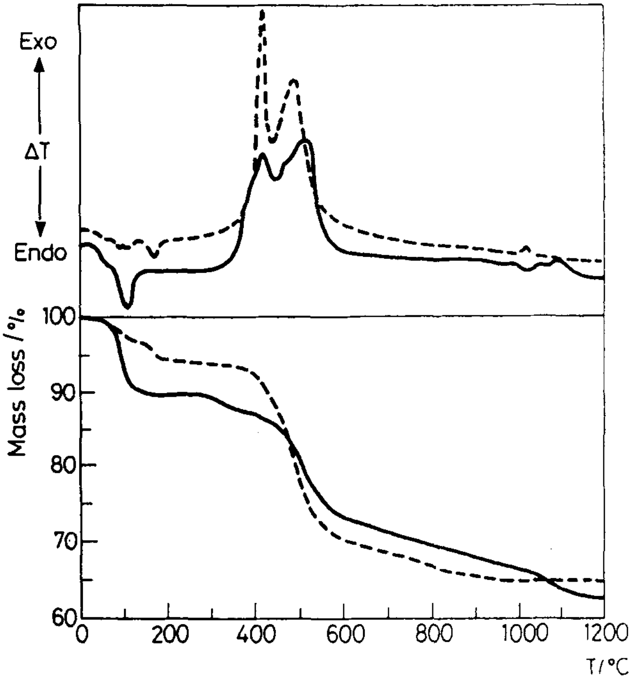

Fig. 4 TG and DTA curves of α-ZrPdmp$_{0.48}$ and γ-ZrPdmp$_{0.45}$ (dotted lines)

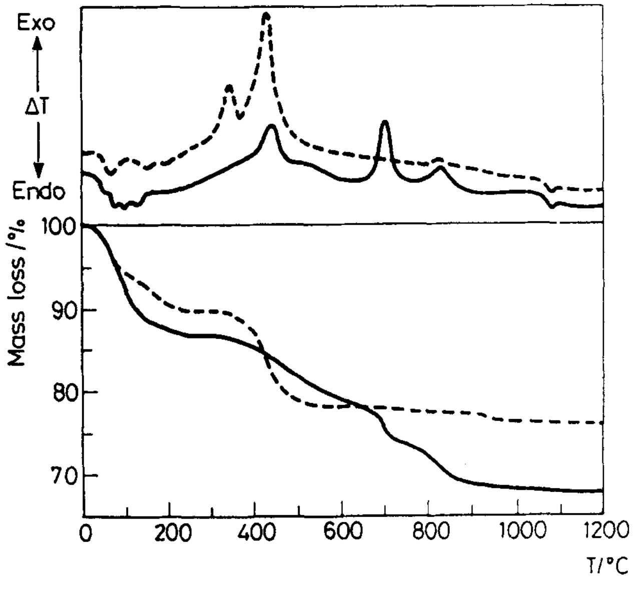

Fig. 5 TG and DTA curves of α-ZrP[Cu(I)-dmp]$_{0.28}$ and γ-ZrP[Cu(I)-dmp]$_{0.25}$ (dotted lines)

However, when coordination compounds are formed between the layers of α- and γ-ZrP, only 1:1 Cu/dmp complexes are present, differently from what found in solution where 1:2 compounds also exist. This demonstrates the role played by a constrained space (the interlayer region of our exchangers) on a solid state coordination chemistry. Thermal techniques greatly help to understand what is occurring in the redox process undergone by the copper ions when they interact with dmp in the solids. However, in order to have a better insight on this phenomenon all the obtained materials are under XPS spectroscopy investigation.

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Zusammenfassung — Es werden zwei Methoden zur Einlagerung von Kupfer-2,9-dimethyl-1,10-phenanthrolin (DPM) Einlagerungsverbindungen zwischen die Schichten von α-$Zr(HPO_4)_2 \cdot H_2O$ und γ-$Zr(H_2PO_4)(PO_4)\cdot 2H_2O$ beschrieben: die direkte Einlagerung von Cu-DMP-Komplexen oder die "in situ" Bildung von Koordinationsverbindungen. Mit dem ersten Austauscher führen beide Methoden zu ähnlichen Produkten mit praktisch identischen Röntgendiffraktionsbildern. Sie enthalten Cu(II-I)-DMP-Komplexe, welche den Feststoffen anfänglich eine grüne

Farbe verleihen, die mit der Zeit oder der Temperatur allmählich ins Gelbe übergeht, wenn die Reduktion von Cu(II) zu Ci(I) vollständig vollzogen ist. Bei γ-$ZrP(H_2PO_4)(PO_4)\cdot 2H_2O$ hat man nur mit der direkten Einlagerung Erfolg. TG/DTA-Versuche ermöglichen ein besseres Verständnis des Geschehens in den Substanzen während des Schrittes der Kupferreduktion, in deren Zusammenhang ein starker endothermer Peak und eine Gewichtszunahme beobachtet werden kann. Diese Experimente zeigen auch, wie der Unterschied von Struktur und chemischer Formel der zwei Austauscher das thermische Verhalten der zwei Verbindungsgruppen beeinflußt.