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THERMAL BEHAVIOUR OF TRANSITION METAL-CONTAINING ZIRCONIUM PHOSPHATE

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Abstract

The thermal behaviour of Co(II), Ni(II) and Zn(II)-containing zirconium phosphate of α type was investigated. XRPD analysis revealed that, for the samples containing Co(II) or Ni(II), the first reflection of the solid phase is split into a doublet. In contrast, when Zn(II) is present, a single solid phase system is formed. The thermal behaviour of the materials followed this sequence. For the samples containing Co(II) or Ni(II), phase-transition processes were found and there was also a loss of crystal water, but for the sample containing Zn(II) there was only one endothermic effect, which corresponded to the decomposition of phosphate groups.

Keywords: phosphate, thermal analysis, transition metals, zirconium

Introduction

Crystalline zirconium phosphate containing divalent, first-row transition metal ions is of interest as a catalyst in various reactions. Even so, very few studies have been carried out on the behaviour of such materials. The detailed work on the ion-exchange behaviour of such materials by Ahrland [1, 2], Clearfield [3, 4] and Allulli *et al.* [5] may be highlighted.

We earlier investigated [6] the thermal behaviour of Cu(II)-containing crystalline zirconium phosphate. The findings indicated the need for further work on crystalline zirconium phosphate containing other divalent transition metal ions. With this aim, crystalline zirconium phosphate of α type (α-ZrP) was equilibrated with appropriate solutions of Co(II), Ni(II) or Zn(II) ions. After identification (by XRPD), the thermal behaviour of the samples was investigated. The results are presented in this paper.

Experimental

Preparation

The α-ZrP was prepared by using the fluoro complex method described earlier [7]. This crystalline material was equilibrated with solutions containing various di-

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valent transition metal ions. Stock solutions of metal(II) acetates (0.1 M) were prepared and aliquots were added separately to 3 g of freshly prepared α-ZrP. The quantity of added solution was calculated by taking into account the exchange capacity (metal(II) content added ≈30% of the total quantity) of the material and the volume/solid ratio (50 ml of solution per 5 mmoles of exchanger). The mixtures were stirred during heating to 80°C and equilibrated for 96 h at this temperature at a constant solution level. After equilibration, the precipitate was filtered and dried over $BaCl_2$. The supernatant liquid was stored for analytical determination.

Analytical

The metal(II) contents of the solutions were determined by standard complexometric titration methods [8]. The quantity of ions exchanged was calculated from the difference between the metal(II) contents of the initial and the residual acetate solution.

Identification

The samples were identified by XRPD, using a DRON-2 computer-controlled diffractometer under conditions described elsewhere [9]. The diffractometrical data were evaluated by a 'searching' computer program [10].

Thermal analysis

Thermoanalytical investigations were carried out with a Mettler TA-1-HT computer-controlled thermobalance that simultaneously provided DTA and TG data. The heating rate was chosen to be 5°C min^{-1}; the temperature range was 25–750°C; the reference material was Al_2O_3; ambience: air; the experiment was carried out in a Pt crucible. The data were evaluated by means of a computer program.

Results and discussion

Analytical

Under the given preparation conditions, 104, 145.6 and 170.7 mg of Co(II), Ni(II) and Zn(II), respectively, were fixed per unit molecular of α-ZrP.

Structure

Diffractometrical curves of the investigated samples are shown in Fig. 1. For the Co(II) or Ni(II)-containing samples, the first reflection of the solid phase was split into a doublet. From these, the main phase was identified as the divalent ion-containing material, while the other corresponded to Θ-ZrP (the crystalline form of ZrP without crystal water).

For the main phases, the following data were obtained: d_{002}=0.975 nm (Co) and 1.002 nm (Ni). For the monoclinic cells, the following parameters were calculated: a=0.8100 nm, b=0.7100 nm, c=2.0170 nm and β=104.14° (Co), and a=0.7260 nm,

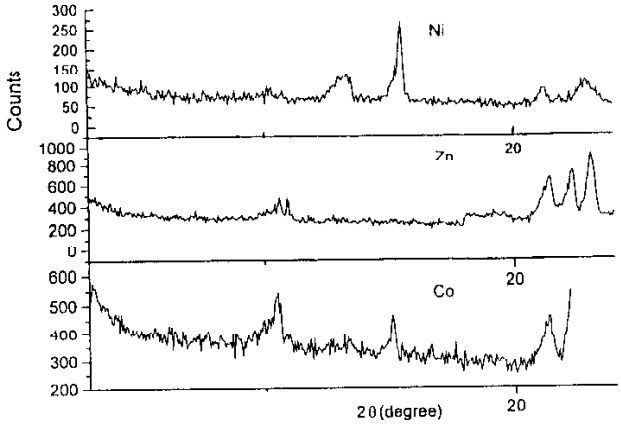

Fig. 1 X-ray curves of investigated samples

b=0.8100 nm, c=2.067 nm and β=96.50° (Ni). In the case of Zn, a single solid phase appeared. Identification of the structures of the products found requires further, more detailed investigations.

Thermal analysis

The curves of the samples are shown in Figs 2–4. The analytical and mass loss data permit the following assumptions:

(1) For the Ni(II)-containing material, three well-defined endothermic processes were distinguished, the second without mass loss. The first can be ascribed to the loss of crystal water (calculations gave 1.5 mole H_2O per unit molecule of α-ZrP), while the third (in the temperature range 260–390°C, with peak at 310°C) is due to the loss of structural water which originates from decomposition of the phosphate groups. For this material, a total mass loss of 14.6% was found.

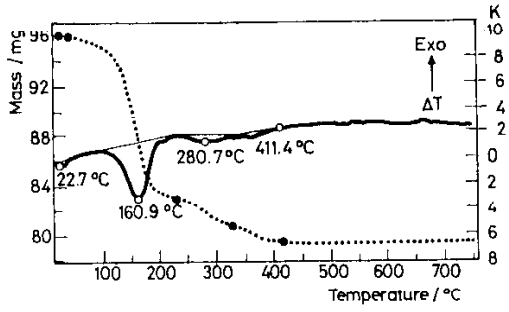

Fig. 2 Thermoanalytical curve of Co(II)-containing α-ZrP

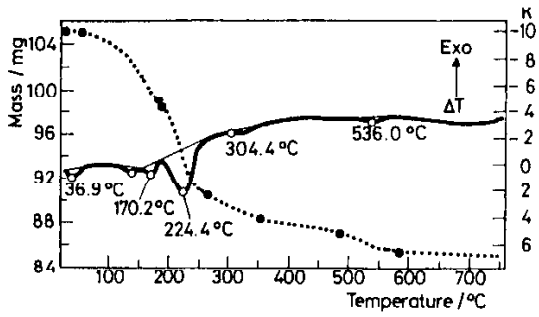

Fig. 3 Thermoanalytical curve of Ni(II)-containing α-ZrP

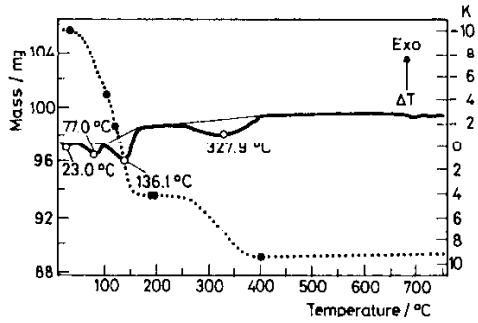

Fig. 4 Thermoanalytical curve of Zn(II)-containing α-ZrP

(2) In the case of the Co(II)-containing material, four endothermic processes were found, the second and fourth without mass loss. These processes can be interpreted as phase-transition processes. The former involves the conversion of the α to the ζ crystalline phase, with an interlayer distance d_{002}=0.45 nm [11]. The latter process is connected with another phase transition, which takes place when the metal (Co) pyrophosphate decomposes to metal oxide and pyrophosphate. Of the endothermic processes involving mass loss, the first can be ascribed to the loss of crystal water (the calculations gave 0.5 mole H_2O per unit molecule of α-ZrP); the third process (in the temperature range 250–500°C, with a peak at 415°C) is due to the loss of structural water originating from decomposition of the phosphate groups. For this sample a total mass loss of 18.2% was found.

(3) The Zn(II)-containing material behaves quite differently. The resulting structure could not be identified as that of any of the known crystalline forms of zirconium phosphate. To solve this problem, further investigations are needed. The endothermic process with mass loss in the temperature range 380–550°C, with peak at 465°C, can unambiguously be ascribed to the loss of structural water (a total mass loss of 8.2% was found), which originates from decomposition of the phosphate

groups. It was presumed that, in the presence of Zn(II) ions during the preparation, α-ZrP first undergoes strong dehydration, giving rise to a new, so far unidentified crystalline phase, containing phosphate groups, as revealed by the thermal analytical data.

Conclusions

It was concluded that the investigated samples have different structures, in consequence of which they exhibit different thermal behaviour. On the basis of the results of analytical methods applied in parallel, and also the mass loss data on the investigated samples, the following compositions are proposed:

$ZrNi_{0.48}(HPO_4)_2 \cdot 2.5H_2O$, $ZrCo_{0.34}(HPO_4)_2 \cdot H_2O$ and $ZrZn_{0.57}(HPO_4)_2 \cdot 2.5H_2O$.

The endothermic processes observed were identified by means of thermal analysis; the processes without mass loss were connected with crystalline phase transitions, whereas those with mass loss were connected with the crystal and structural water loss. From the determined total mass losses (13.0, 6.6 and 12.5%, respectively), the quantity of crystal water was calculated as 2.5, 1.0 and 2.5 mole H_2O per molecule unit of α-ZrP, respectively.

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