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Dehydration behavior of some microporous zincophosphates

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Abstract

The dehydration behavior of two synthetic, unsubstituted and cobalt-substituted, zincophosphates (one a sodalite analog and the other a new, hexagonal phase) was studied by TG/DTG and DSC. TG/DTG curves of the sodalite phases were very similar, exhibiting only one major weight loss that shifted to higher temperatures with increased amount of cobalt substitution. The profiles of the corresponding DSC curves, however, differed considerably among themselves. TG/DTG curves of hexagonal phases showed a more complex, multi-step dehydration behavior; the corresponding DSC curves also exhibited multiple endotherms.

An explanation of these phenomena is given in terms of the specific arrangement of water molecules within a particular zincophosphate framework.

Keywords: Cobalt-Zincophosphates; Dehydration; TG–DTG–DSC; Zincophosphates

1. Introduction

Microporous solids belong to a very important class of materials because of their great potential for a variety of applications, including adsorbents, ion exchangers, and catalysts [1–3]. Aluminosilicates (zeolites) and aluminophosphates [4] are the best known of these, although some other compounds [5–8] can also adopt open-framework structures. Zinc phosphates, for example, have a well-established chemistry, but

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until now it has not been known that open-framework zincophosphates can exist. Stucky and co-workers [9–11] have recently prepared a number of porous zincophosphates. Some of them are zeolite analogs whereas others represent novel structural types.

Modification of an open-framework lattice by isomorphous replacement of domain cations by heteroatoms (especially transition metals [12]) can provide the opportunity for tailoring materials with desired properties, i.e. enhanced catalytic activity and selectivity [13–14]. With respect to this, we have investigated the influence of cobalt(II) incorporation in two different porous zincophosphates on their thermal behavior.

2. Experimental

The studied zincophosphates were synthesized by the crystallization of gel with the following composition: $1.75Na_2O : xCoO : (1-x)ZnO : 0.625P_2O_5 : 160H_2O$, where x was 0, 0.1 and 0.2. The crystallization was carried out at atmospheric pressure and temperature. Depending on the method by which the reactants were mixed (either by vigorous stirring or by slow, careful addition), two zincophosphate phases were obtained: a novel, hexagonal phase (abbreviated to HEX) and a sodalite analog (abbreviated to SOD). The procedure details will be published elsewhere. The crystalline products of the obtained phases exhibit different morphologies and crystal sizes as illustrated in Fig. 1.

The composition of the obtained phases corresponds to a common formula which can generally be written as $Na_6[Co_xZn_{1-x}PO_4]_6 \cdot yH_2O$, where x equals 0, 0.1 and 0.2. The content of water depends on the product's structure as well as on the amount of cobalt component (see below).

3. Instrumentation

The crystallinity of the products was checked by X-ray powder diffraction using a Philips PW 1710 diffractometer (Cu Kα radiation). Elemental analyses were determined by inductively coupled plasma emission spectroscopy. Thermal analysis measurements were performed using TG 951 and DSC 910 modules of the TA2000 thermal analyzer (TA Instruments, Inc.). Samples were heated from 25 to 350°C at a heating rate of 10°C min^{-1} under a helium flow of 50 ml min^{-1}. ^{31}P NMR spectra were obtained on a Varian VXR-300 spectrometer at a frequency of 121.415 MHz at a spinning rate of 4–5 kHz.

4. Results

TG curves of the SOD samples are given in Fig. 2. The samples exhibit similar thermal behavior, that is, ZnPO, CoZnPO ($x = 0.1$), and CoZnPO ($x = 0.2$) show only one weight loss. This weight loss can be attributed to the removal of eight water

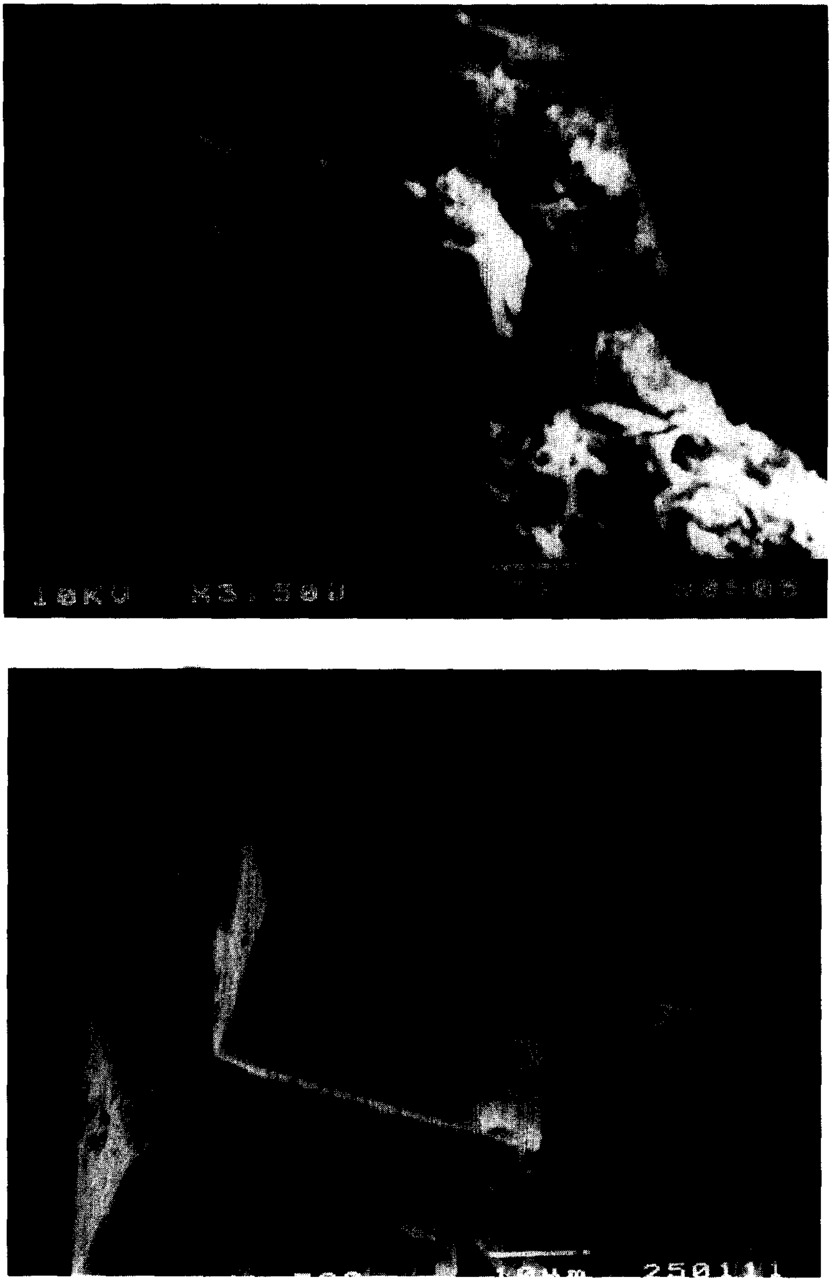

Fig. 1. SEM micrographs of the morphology and crystal size of the ZnPO-SOD (upper) and ZnPO-HEX (lower) phases.

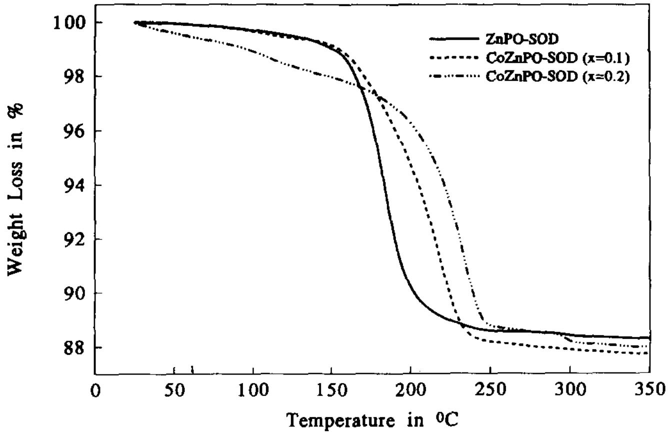

Fig. 2. TG curves of SOD samples.

molecules from the sodalite framework. It is well known that sodium cations and water molecules, trapped in a sodalite cage, i.e. a β- cage, form $Na_3(H_2O)_4$ species which probably make H-bond contacts with framework oxygen atoms. Thus, it seems likely that the linkages of water molecules inside the species are all equivalent. At the same time, cobalt incorporation in the sodalite zincophosphate framework does not influence the water arrangement. However, CoZnPO samples exhibit a small weight loss (≈0.5%) below 80°C which is most likely due to water (the amount of which corresponds to 0.5 molecule) physically sorbed on the surface.

The shapes of the DTG curves (Fig. 3) confirm the continuous character of the mass loss since they exhibit only one major maximum. The position of the maximum shifts to higher temperatures when the amount of cobalt in the sample increases.

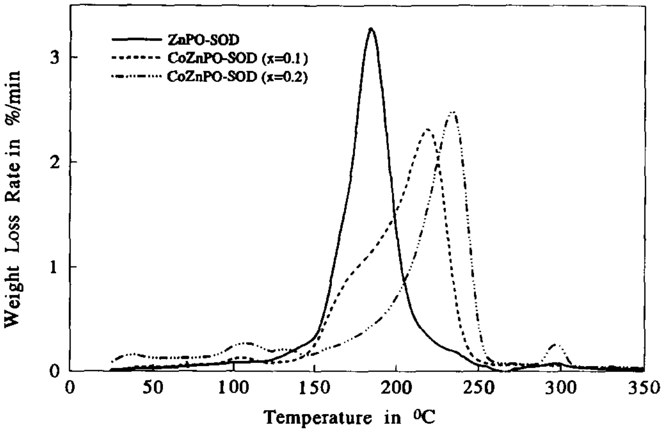

Fig. 3. DTG curves of SOD samples.

DSC curves are given in Fig. 4. The ZnPO sample shows a single sharp endotherm at 155°C. The endotherms of the CoZnPO samples, however, appear at higher temperatures. Furthermore, their profiles are quite different. For the sample with $x = 0.1$, the broad endotherm was deconvoluted [15] into three Gaussian peaks at 158, 167 and 189°C, whereas for CoZnPO with $x = 0.2$, the deconvolution indicated two peaks at 181 and 215°C. These differences can be explained as follows. Replacement of zinc atoms by more electronegative cobalt (II) affects the strength of the H-bond contacts between $Na_3(H_2O)_4$ species and cobalt-substituted zincophosphate lattice. Furthermore, differences among the samples with varying amounts of cobalt substitution indicate that Co distribution over the Zn sites is not completely random.

TG and DTG curves of HEX samples are illustrated in Figs. 5 and 6, respectively. The shapes of these TGA curves are significantly different from the TGA curves for SOD products. The water molecules gradually release from the hexagonal phase, thus indicating a different arrangement of the water molecules. Structural data confirm this suggestion. In contrast to sodalite zincophosphate, the hexagonal phase possesses a helix, built up of sodium cations and water molecules, which is stabilized inside the framework.

The amount of water, however, depends on the amount of cobalt component. For ZnPO product, there are 7 H_2O molecules per $Na_6[ZnPO_4]_6$ unit whereas CoZnPO ($x = 0.1$) possesses 8 H_2O molecules and CoZnPO ($x = 0.2$) has 9 H_2O molecules. Similar to the products with sodalite structure, replacement of zinc by cobalt (II) also affects the dehydration process. However, DTG maxima are at lower temperatures for CoZnPO samples than for the ZnPo sample. This effect may be related to the helix arrangement of the water molecules. DSC curves (Fig. 7) also exhibit several endotherms corresponding to different stages of water removal.

It is interesting that only the DSC curve of the ZnPO sample shows an exotherm at 289°C which can be attributed to the phase transformation of the hexagonal network.

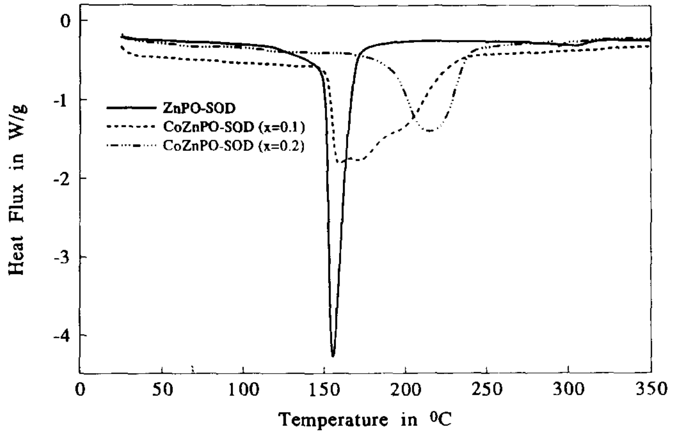

Fig. 4. DSC curves of SOD samples.

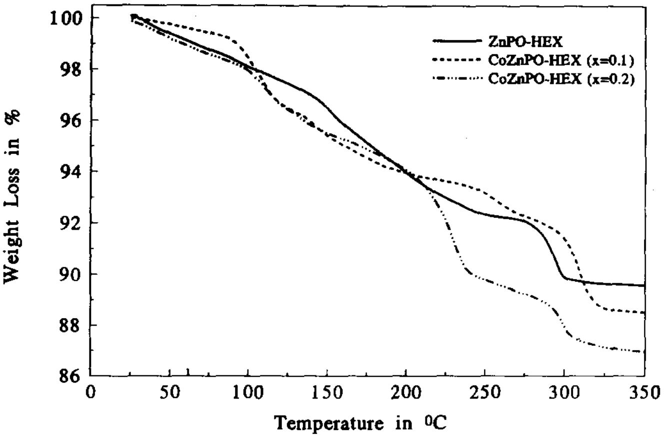

Fig. 5. TG curves of HEX samples.

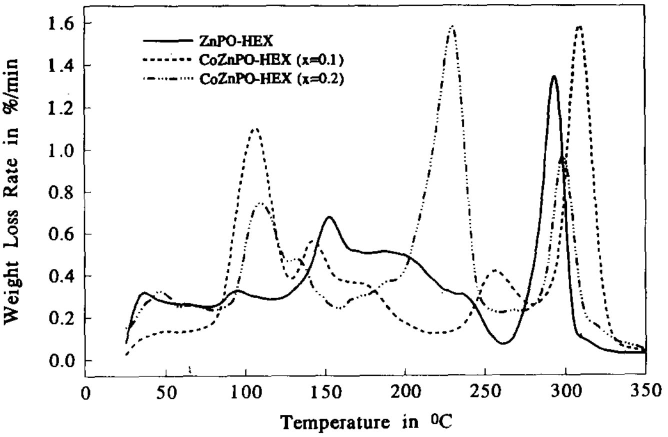

Fig. 6. DTG curves of HEX samples.

It is evident from the X-ray diffraction scans that neither crystalline system retains their structure after complete dehydration. The sodalite products and the hexagonal products transform into the same new crystalline phase (Fig. 8). This intriguing fact is still a subject to debate.

Concerning the ^{31}P MAS NMR measurements, this novel dehydrated crystalline phase shows two sharp peaks at 8.4 and 11.2 ppm, relative to H_3PO_4, with an intensity ratio of 1:4. This could be attributed to the different crystallographic phosphorous sites within the unknown structure. However, any detailed assignment of the ^{31}P signals is difficult in the absence of precise structural information.

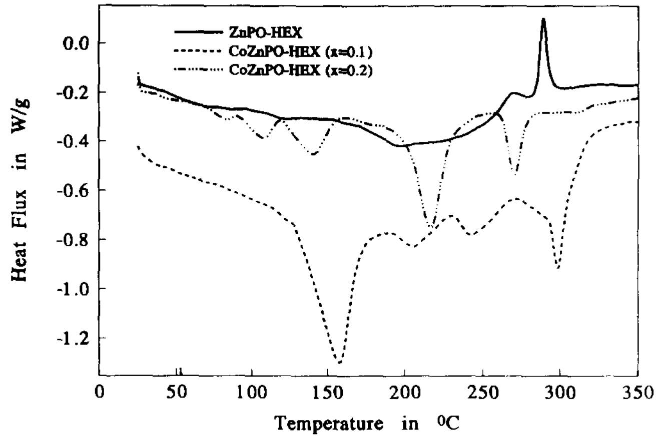

Fig. 7. DSC curves of HEX samples.

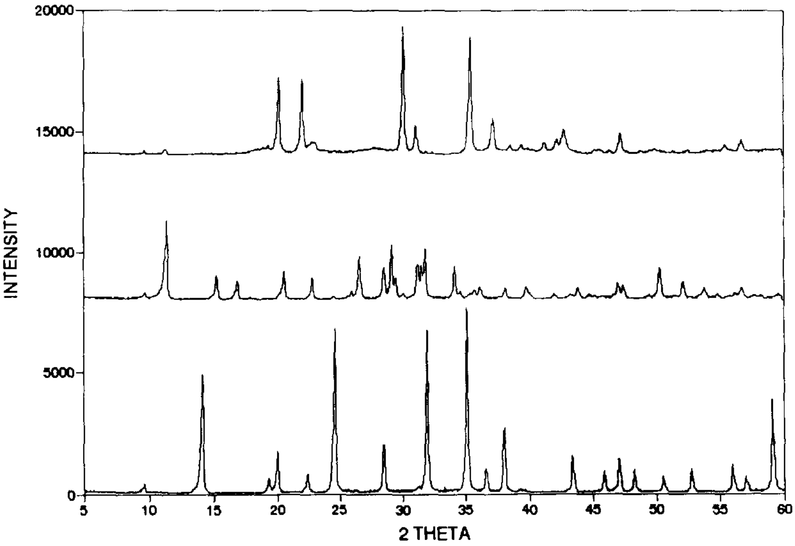

Fig 8. X-ray diffraction traces of ZnPO-SOD (lower), ZnPO-HEX (middle), and their dehydrated phase (upper).

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