

Thermal investigations of some AlPO and MeAPO materials prepared in the presence of HF

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Abstract

Hydrothermal synthesis of chabazite-like AlPO₄ in a fluoride medium, using piperidine as the structure directing agent, is also successful in the preparation of transition-metal-modified AlPO products. The transition metal (Co, Mn, and Ni) has no influence on the triclinic deformation of the chabazite framework, formed by an interaction of fluoride ions with the AlPO framework. Upon calcination, successive destruction of piperidine and fluoride bridges occurs. The calcined chabazite-like products exhibit a particular sensitivity for humidity resulting in a new triclinic deformation of the chabazite framework. The deformation is completely reversible and can be removed by dehydration. The transition-metal incorporation exerts an influence on the dehydration process. © 1997 Elsevier Science B.V.

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1. Introduction

Several new classes of molecular sieves have been reported in the last decade. They include aluminophosphates [1] (AlPO₄-*n*, where *n* denotes a specific structure type), silicoaluminophosphates [2] (SAPO-*n*) and metal-substituted aluminophosphates [3] (MeAPO-*n*). Among the AlPO family, some members possess structures analogous to those of zeolites (e.g. the structure type 34 is analogous to the naturally occurring zeolite chabazite), whereas others are novel (e.g. AlPO₄-5 has no naturally occurring counterpart).

Generally, aluminophosphate-based microporous solids have been synthesised from gels containing sources of aluminium, phosphorous, and at least one organic amine (as the structure directing agent). Thus, several organic amines have been successfully used as templates [4–6] in the preparation of element-modified AlPO₄-34 (SAPO, MeAPO or MeAPSO-34). However, attempts to produce AlPO₄-34 itself (under identical conditions) have been unsuccessful.

Recently, Kessler et al. [7,8] found that an addition of HF to the reaction mixture (with morpholine as the structure-directing agent) made it possible to obtain AlPO₄-34 (more exactly, a precursor of AlPO₄-34, vide infra). They suggested that HF had at least two roles: (1) the fluoride ions solubilise aluminium lead-

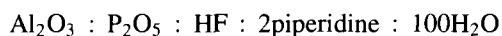
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ing to a slower nucleation (thus, rendering the formation of dense aluminophosphates less favourable), and (2) the fluoride ions impart also templating effect. It has been found that fluoride ions interacted with the framework (i.e. bridging some of the Al atoms) causing a triclinic deformation of the rhombohedral chabazite structure [9]. Calcination of the as-synthesised, triclinic AlPO_4 resulted in the destruction of fluoride bridges and obtaining the chabazite-like AlPO_4 material (AlPO_4 -34).

The aim of this work was to investigate the thermal behaviour of AlPO_4 and metal-modified AlPO_4 (MeAPO ; Me = Co, Mn, Ni) prepared with piperidine as a structure-directing agent in the presence of HF. Chabazite-like aluminophosphates are interesting because they have been found very active as catalysts and adsorbents [10–12].

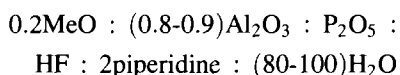
2. Experimental

The reactants used were piperidine (99%, Aldrich), 85% phosphoric acid (Fluka), 40% hydrofluoric acid (Fluka), aluminium isopropoxide (Aldrich), and cobalt(II), manganese(II) and nickel(II) acetates (Merck). The relative molar composition of the reaction mixture used in the preparation of AlPO_4 -34 was:



The mixture was prepared by successive additions of phosphoric acid, hydrofluoric acid and piperidine to the suspension of aluminium isopropoxide in water during vigorous stirring.

MeAPO -34 products were prepared using a batch composition of:



The reaction mixture was prepared in the following manner: To a finely dispersed water suspension of aluminium isopropoxide (with a water content about 2/3 of that required by the above composition), the following components were successively added: appropriate metal acetate (dissolved in the remaining amount of water), phosphoric acid, hydrofluoric acid, and piperidine. The system was thoroughly blended (by using an Ultra-Turrax T 25; Janke and Kunkel

GmbH) to a homogeneous mixture each time prior to the addition of the next component.

The crystallisation was performed in the usual way (stainless-steel Teflon-lined pressure vessels; 190°C, from two-to-four days) under static conditions. The products were recovered by centrifugation, washed with distilled water and dried at 105°C. As-synthesised materials exhibited different colours, depending on the reaction mixture composition. In the case of aluminophosphate and manganese-containing reaction mixtures, colourless products were obtained. Crystallisation of cobalt- and nickel-containing reaction mixtures yielded royal blue and pale blue products, respectively.

3. Instrumentation

The morphology of products obtained was studied by scanning electron microscope (Jeol JSM-T220). Elemental analyses were obtained by inductively coupled plasma emission spectroscopy. Carbon, hydrogen and nitrogen were determined with a standard C–H–N analyser. The crystallinity of the products was checked by X-ray powder diffraction using a Phillips PW 1710 diffractometer with CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$). Diffuse reflectance spectra were obtained on a Varian MS 80 UV/VIS spectrophotometer in the 800–300 nm range, with MgO as a standard. Thermal analyses were carried out on a TA2000 instrument (using TG 951 and DSC 910 modules). Samples were heated from 25 to 1000°C at a heating rate of 10°C/min under a helium flow of 50 ml/min.

4. Results

The XRD patterns of all products showed the materials to be crystallographically pure triclinic chabazite-like AlPO_4 -34 (7). No evidence of an amorphous phase was found. Scanning electron micrographs also showed that materials were highly crystalline (no indication of impurity phases could be detected). The crystals exhibited the cube-like morphology typical of chabazite-like materials. Moreover, no distinct dependence of the crystal habit or size on the presence of transition-metal cations could be

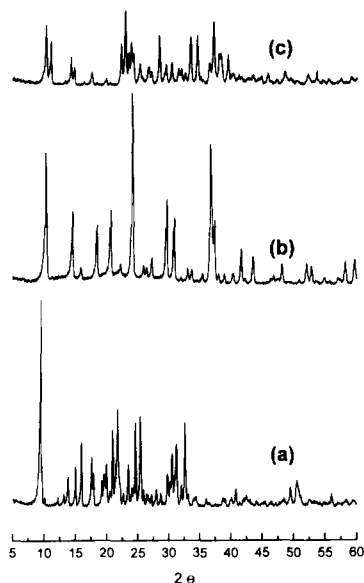
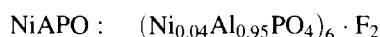
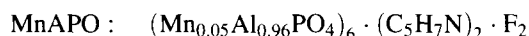
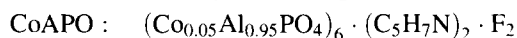
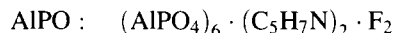


Fig. 1. X-ray powder diffraction patterns of: (a) – as-synthesised AlPO_4 ; (b) – calcined AlPO_4 ; and (c) rehydrated calcined AlPO_4 .

found. A representative diffractogram and a scanning electron micrograph are presented in Figs. 1 and 2, respectively.

Elemental analyses of the as-synthesised materials when using TGA results and the C–H–N analyses gave the following product compositions:



The compositions of the samples were calculated for TO_2 formula on an anhydrous basis. The results of chemical analyses reveal a transition-metal substitution of aluminium. For all MeAPO products, the balance $\text{Al} + \text{Me} = \text{P}$ lies within experimental error range. This is also in accordance with the majority of results from diffuse reflectance spectroscopy: diffuse reflectance spectrum¹ of the Co-containing product entirely corresponds to tetrahedrally coordinated Co(II) indicating a Co/Al framework substitution. In the case of Ni-containing product, the diffuse reflectance spectrum (shown in Fig. 3(a)) exhibits main

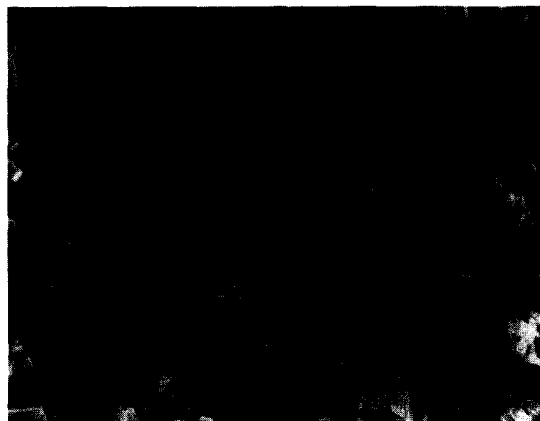


Fig. 2. Scanning electron micrographs of as-synthesised AlPO_4 .

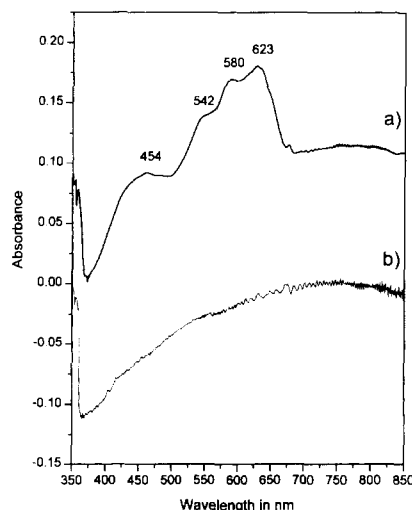


Fig. 3. Diffuse reflectance spectra of: (a) – NiAPO; and (b) – MnAPO products.

absorption bands that most likely correspond to Ni(II) cations in a distorted tetrahedral symmetry [14]. This fact, in this case, leads to the conclusion that Ni(II) cations are also the constituents of the AlPO framework (i.e. they replaced framework Al). For the Mn-containing product, the diffuse reflectance spectroscopy, in general, is not a very informative method, because the electronic spectra of Mn(II) are mainly broad (Fig. 3(b)), so that one cannot make a very clear distinction between tetrahedral and octahedral coordination geometry. Thus, for Mn-containing product, only the elemental analysis has been a proof of the incorporation of Mn(II) into the AlPO skeleton. How-

¹The spectrum has been reported elsewhere [13].

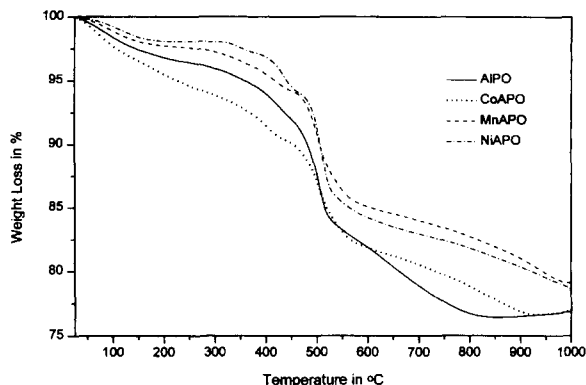


Fig. 4. TGA profiles of AlPO_4 and various MeAPO products.

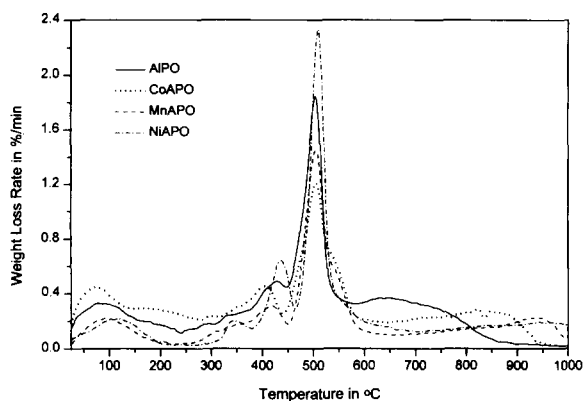


Fig. 5. DTG profiles of AlPO_4 and various MeAPO products.

ever, it can be added that some preliminary data on cyclic voltammetry investigations² offer a firm support for the manganese(II) framework substitution.

TGA and DTG profiles (Figs. 4 and 5, respectively) are not significantly different for various products. Generally, there are three weight losses corresponding to water desorption, piperidine decomposition and fluoride bridges cleavage. The first weight loss (up to ca. 250°C) is due to water which is not only physically sorbed on the surface but also bound in the cages. Only for the CoAPO material, a clear difference between water physically sorbed and the water bound to the framework can be observed: in the region attributed to the water loss there are two DTG minima, indicating a noncontinuous character of water loss (Fig. 5).

²The results will be published elsewhere.

The second weight loss (up to ca. 600°C) can be attributed to the piperidine decomposition. In this region, all products exhibit almost the same shape of DTG curves. This indicates that the template removal does not depend on the transition-metal substitution. For all products, only one DTG minimum (corresponding to the maximum decomposition rate) can be observed at ca. 450°C. The third weight loss may be related to fluoride evolution. For AlPO product, the third weight loss is terminated at ca. 870°C. However, for MeAPO materials the process is completed at a higher temperature (ca. 1000°C). The difficulty in removing fluoride from MeAPO framework might be related to the stronger Al–F–Al bonds in triclinic MeAPO than in the triclinic AlPO framework. This observation has at least two consequences: (1) it lends additional support to the conclusion that the transition metals are real constituents of the AlPO skeleton; and (2) transition-metal distribution is not entirely random.

DSC profiles of the AlPO and MeAPO are given in Fig. 6. It can be seen that the products exhibit similar thermal behaviour. Up to 600°C, several endotherms can be found, corresponding to water loss and template removal. The first broad endotherm at ca. 100°C is due to water evolution while the remaining ones correspond to piperidine decomposition. It can be seen that template removal proceeds in four stages: at ca. 340°, 420°, 440° and 500°C. Furthermore, the temperature of the endotherms does not correlate with the transition-metal incorporation into the AlPO skeleton.

The XRD diagrams of all calcined samples show the characteristic pattern of the CHA structure (Fig. 1(b)).

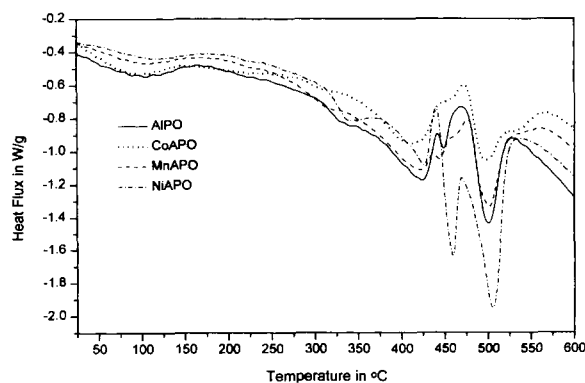


Fig. 6. DSC profiles of AlPO_4 and various MeAPO products.

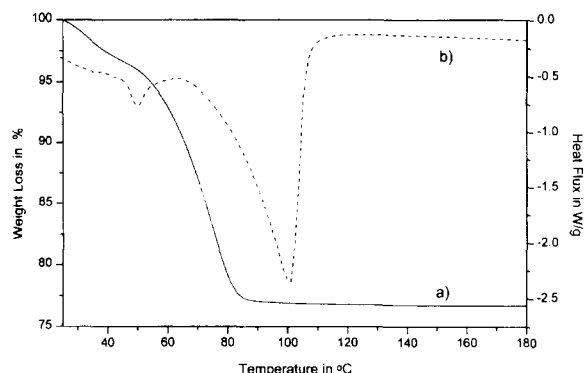


Fig. 7. Dehydration of rehydrated calcined AlPO_4 : (a) TG – analysis; and (b) – DSC analysis.

However, in contrast to chabazite material prepared in nonfluoride medium, the products synthesised in this work rapidly adsorb water from the atmosphere at room temperature. The calcined CoAPO and MnAPO also change their colour, indicating their redox behaviour [13]. This particular sensitivity to humidity is accompanied by the deformation of chabazite framework. The hydrated calcined samples exhibit the XRD pattern different from that of the dried ones (Fig. 1(c)). However, this phenomenon is completely reversible: the dehydration causes a complete transformation to the chabazite framework. Thus, we also investigated thermal behaviour of the fully hydrated³ AlPO and MeAPO products.

The TG/DTG-DSC curves of all the hydrated materials exhibit a similar shape. Typical TG and DSC curves are given in Fig. 7(a) and (b), respectively. The first weight loss is accompanied by an endotherm at ca. 70°C ; it is due to the water physically sorbed on the surface. The second weight loss can be attributed to water bound in the channels/cages. The corresponding endotherm can be resolved into three endotherms, indicating water loss from different crystallographic sites.

Preliminary crystallographic studies⁴ indicate that in fully hydrated products the water molecules

³The materials were digested under a saturated NH_4Cl solution in the course of five days.

⁴Synchrotron X-ray powder diffraction analysis is in progress. Rietveld refinement gives a triclinic unit cell for the hydrated AlPO_4 . However, the triclinic deformation differs from that caused by the fluoride bridges.

Table 1

Results of TG-DSC analyses of fully hydrated AlPO and MeAPO products

Product	Total weight loss, %	T_1^a C	T_2^a C	T_3^a C	T_4^a C
AlPO_4	20.0	74	104	118	124
CoAPO	19.2	69	104	115	119
MnAPO	19.9	74	110	123	129
NiAPO	20.2	71	100	115	122

^a T_2 – T_4 are obtained by fitting the peak of the second endotherm by three Gaussian functions.

interact not only with framework oxygens (via H-bonds) but also with the Al atoms of the skeleton (a consequence of this is the deformation of the tetrahedral chabazite framework, vide supra). The TG-DSC results are given in Table 1. Transition-metal incorporation into the AlPO skeleton causes a decrease of the dehydration temperature for the CoAPO and NiAPO products. For the MnAPO solid, an increase of the second endotherm-dehydration temperature is observed. This might be due to the fact that, upon hydration, water molecules interact not only with aluminium atoms but also with manganese atoms.

In summary, the fluoride route of synthesis AlPO_4 -34 is also successful in the preparation of its transition-metal modified products. The transition metal (Co, Mn and Ni) exerts no influence on the triclinic deformation of the rhombohedral chabazite framework, given that fluoride ions that have been found to interact with the AlPO skeleton, deform MeAPO 's framework in the same manner (forming also the Al-F-Al bridges). When fluoride bridges have been removed (upon calcination), the chabazite products exhibit a particular sensitivity to humidity, water molecules interacting with a skeleton cause a new (triclinic) deformation of the framework. The deformation is completely reversible and can be removed by dehydration. The dehydration process, however, does depend on the transition metal incorporation. For CoAPO and NiAPO products, the dehydration occurs at a temperature lower than that for AlPO_4 . For MnAPO , the dehydration temperature increases, indicating that the hydration proceeds in a different manner, and depends on transition-metal incorporation.

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