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Burning out of di-*n*-propylamine template from MeAPO-31 materials studied by thermal analysis

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Abstract

Conditions for oxidative burning out of template, di-*n*-propylamine, from MeAPO-31 materials have been studied by means of thermal analysis. The materials were doped with very low amounts of Cu, Cd, Co, Mn, Mg, and Zn, ranging from 0.04 to 0.63 wt.%. These low contents of heteroatoms have significantly determined the observed effects. The same holds for the stability of the microporous ATO (aluminophosphate thirty-one) type structure. Grinding of the crystallites leads to more efficient exchange of atmosphere and the gaseous products and thus results in a tendency to lower calcination temperature. This observation may be useful when considering a lower thermal stability of higher doped microporous MeAPO-31 materials.

Keywords: Calcination; Heteroatoms; MeAPO-31; Thermal analysis; Thermal stability

1. Introduction

Microporous aluminophosphates ($AlPO_4$-*n*) [1] and their heteroatoms containing derivatives (MeAPO-*n*) [2] are synthesized in the presence of structure-directing templates, mostly amines. The latter, together with water molecules, remain embedded within the pore systems of the synthesized solids. Therefore, prior to an application of these molecular sieves for, e.g. permeation [3,4] or optical [5,6] techniques, water and templates have to be removed from the pores. The easiest method is calcination under an oxidizing atmosphere [7].

For preventing the pore structures from a damage or even collapse, suitable treatment conditions should be found at first. This can best be done with TG–DTA measurements of the template release and temperature-programmed X-ray diffraction (XRD) investigations which are able to indicate possible phase transformations.

Aiming at this, we studied the effect of various amounts of two-valent ions of heterometals (Me) incorporated into the framework on (i) structure symmetry, (ii) structure stability [8], and (iii) detemplating mechanisms [9] of the MeAPO-31 samples. Concerning these topics, the chosen system has not been studied so far. Two papers [10,11] have been focused on incorporation of various heteroelements into $AlPO_4$-31 with respect of generating catalytic active centers. This aluminophosphate structure (aluminophosphate thirty-one (ATO) type [12], 36 T-atoms per unit cell (u.c.)) forms unidimensional pores of 0.54 nm diameter. Therefore, a temperature-forced exiting of the enclosed template molecules should not be impeded.

In contrast to most of the studied MeAPO-*n* systems (e.g. [13–25]), we examined the samples doped only with very low amounts of metals Cu, Cd, Co, Mn, Mg, and Zn. Thus, a more perfect incorporation of the metals into the skeletons was expected. Moreover, higher amounts might partially form extra-framework metal species in the pores

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Table 1
MeAPO-31 materials and thermal analysis data

Sample no.	Me	Reaction gel no.[a]	Me (wt.%)	u.c./Me	Structure collapse (K)	P1 (K)	P2 (K)	F^{b}
0	–	–	–	–	>1323	508	–	–
1	Cu	2	0.039	74.1	1323	513	788	0.95
2	Cd	2	0.083	61.7	1303	508	783	0.97
3	Co	1	0.092	29.1	1303	508	793	1.20
4	Mn	1	0.113	22.1	1253	518	798	1.26
5	Co	2	0.174	15.4	1263	508	808	1.56
6	Co	2	0.182	14.8	1253	523	813	1.69
7	Mg	1	0.078	14.2	1253	513	803	1.37
8	Zn	1	0.223	13.0	1223	518	803	1.55
9	Mn	2	0.212	11.8	1203	513	813	1.88
10	Mn	2	0.216	11.6	1233	518	813	1.60
11	Zn	1	0.304	9.8	1203	513	823	1.80
12	Mg	2	0.145	7.6	1183	513	823	1.77
13	Mg	2	0.152	7.3	1193	518	833	1.86
14	Zn	2	0.552	5.4	1103	518	838	2.21
15	Zn	2	0.634	4.7	–	518	843	2.31

[a] See Section 2.
[b] F is intensity ratio of $R2$ to $R1$.

apart from incorporation as, e.g. in the MeAPO-34 materials [26].

The results of the TG and DTA investigations of burning out of di-*n*-propylamine from the studied MeAPO-31 samples are presented and the observed effects discussed.

2. Experimental

2.1. Methods

The samples were examined by X-ray diffraction, temperature-programmed XRD (Guinier technique), light and scanning electron microscopy (SEM), and inductively coupled plasma (IPC) trace analysis (for details see [8]). Thermoanalytical measurements were performed by the following techniques:

- *Method* 1: TG measurements were carried out with a Mettler TA 3000/TG50 instrument. The samples (masses about 15 mg) were heated up from 300 to 1273 K at a rate of 10 K/min under flowing oxygen. All samples passed through this method.
- *Method* 2: TG and DTA profiles were recorded simultaneously by a thermobalance SETARAM TAG 24 coupled with a mass spectrometer Thermostar (Balzers) to analyze evolving gases. The reduced molecular masses (m/z) from 12 to about 180 could be detected. Samples of about 20 mg were heated from room temperature to 1373 K at a rate of 5 K/min under a flowing air/argon

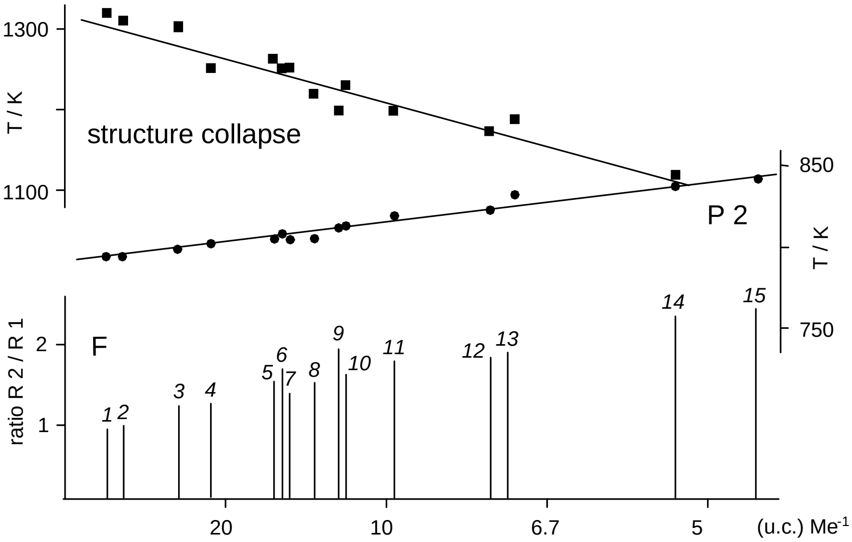

Fig. 1. Thermal stability of ATO type materials (temperature of structure collapse), temperature of the thermogravimetric P2 peak, and intensity ratios of the regions $R2$ to $R1$ in dependence on the heteroatom content, u.c./Me.

mixture. This method was restricted to some selected samples.

2.2. Synthesis of the MeAPO-31 materials

Hydrothermal syntheses were done from reaction gels with the component ratios (as oxides) of 1 Al_2O_3:1 P_2O_5:a MeO:1.7 DPA:280 H_2O, where $a = 0.005$ (reaction gel 1), or $a = 0.01$ (reaction gel 2), DPA denotes di-*n*-propylamine, MeO sulphates of divalent Cu, Cd, Mn, Co, Mg, and Zn. P_2O_5 stands for H_3PO_4 (85 mass%), and Al_2O_3 for a pseudo-boehmite-like aluminium oxide hydrate sol of the content of 2.35 mass% of Al_2O_3, purchased from VEB Säureschutz, Berlin. The other materials were analytical grade reagents from Merck and bidistilled water. The gels of pH = 3.5 ± 0.2 were reacted in Teflon-lined autoclaves at 463 K for 48 h. After cooling down, the crystallized products were washed and worked up (for details see [8]). As a comparison sample, non-substituted $AlPO_4$-31 has also been synthesized.

3. Results and discussion

The synthesized ATO phases, identified by their XRD patterns, consisted of aggregated prismatic crystals about 50 μm long and overgrown along their [0 0 1] axes. Due to a

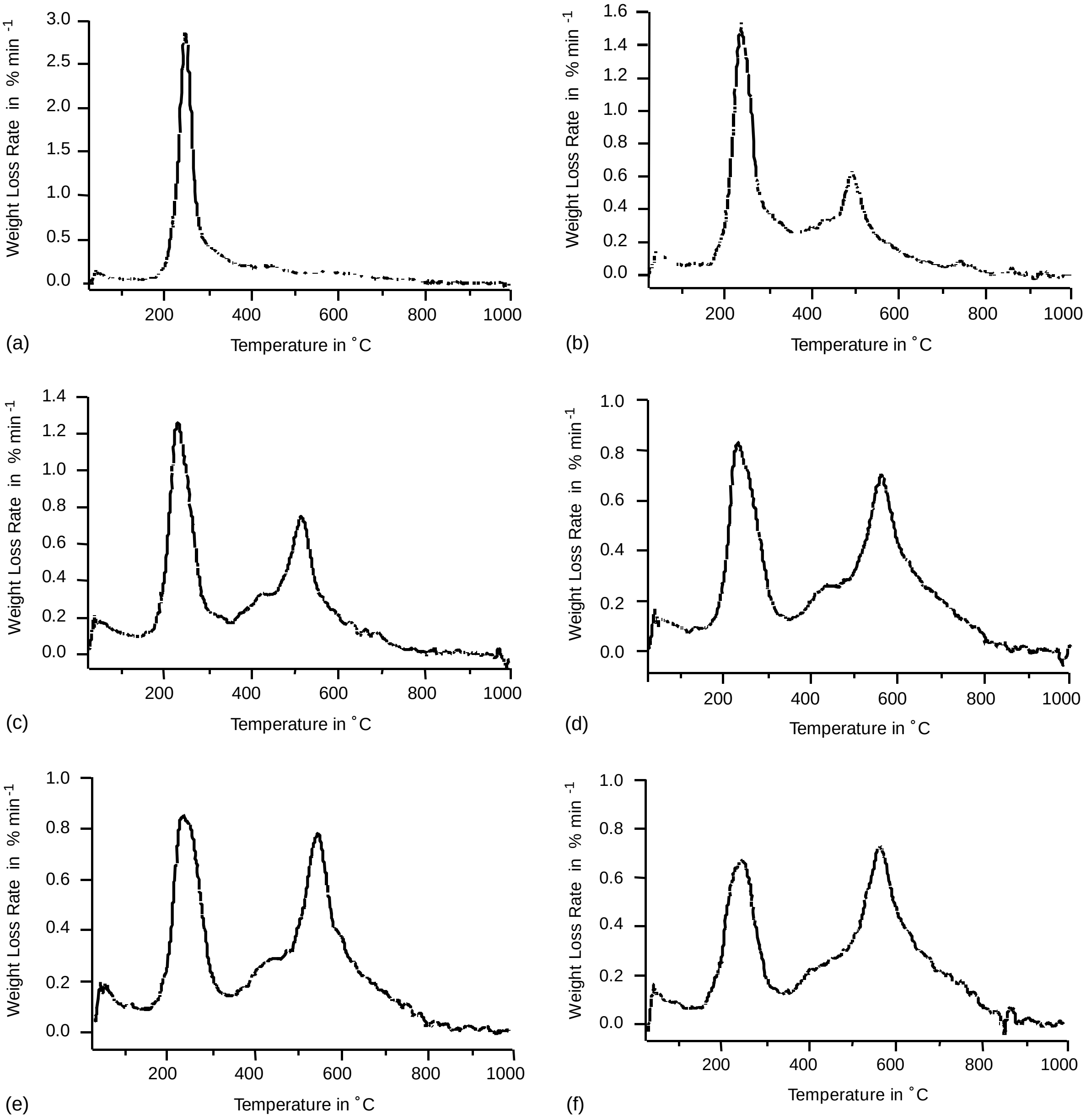

Fig. 2. Examples of the DTG profiles, recorded with the method 1, for samples no.: (a) 0 ($AlPO_4$-31); (b) 1 (CuAPO-31); (c) 3 (CoAPO-31); (d) 12 (MgAPO-31); (e) 11 (ZnAPO-31); (f) 14 (ZnAPO-31).

narrow particle size distribution, an effective separation from differently sized by-products was easily achieved. Thus, the samples of phase purity better than 95 mass% were obtained [8].

As we aimed at, the contents of incorporated heteroatoms differed strongly for the particular metals ranging from 74.1 u.c./Cu to 4.7 u.c./Zn (Table 1). Details and interpretation are given elsewhere [8].

The TG/DTG results (method 1) present a general tendency characteristic of the systems. Two ranges are observed for the main losses of mass under oxidizing atmosphere (Fig. 2), namely

- range *R*1: 425–625 K with a DTG peak P1 at (513 ± 10) K;
- range *R*2: 625–1125 K with a DTG peak P2 at (783–843) K.

In addition, a lower loss of mass occurs below 425 K, which reflects desorption of water from the surfaces of the crystallites being initially dried at 398 K and next kept in contact with open atmosphere for several days.

The total loss of mass between room temperature and 1273 K equals to 8.8±0.2% and is not noticeably influenced by the type and amount of heteroatoms. The summarized losses within the ranges *R*1 and *R*2 amount to 7.2 ± 0.2 mass%. Moreover, the loss of mass shifts dominantly into the range 2 with rising content of heteroatoms (Fig. 2). This is also evident from the systematic increase in the intensity ratio $F = R2/R1$ from 0.95 (CuAPO-31) to 2.3 (ZnAPO-31) (Table 1, Fig. 1). However, it is difficult to differentiate between possible specific influences of the particular heteroelements due to a too low number of samples.

The shifting of the mass loss is caused by the energetic interaction between the adsorption centers (heteroatoms) of the skeleton and the molecules inside the pores, comprising water, template, and those being formed during calcination. Thus, the mobilities of all of them and, in consequence, the removal of template and of the products of cracking and oxidation undergo reduction with increasing number of heteroatoms. Di-*n*-propylamine should probably be the least movable species in the pores. This is to say that the detemplation process is governed by kinetics apart from chemical reactions. These considerations correspond to the rising temperature of the peak P2 (Table 1, Fig. 1), that results from the time delay between the constant heating of the samples and the discussed mobility effects. Choudhary and Sansare [7] have similarly interpreted the removal of tripropylamine from $AlPO_4$-31 as the process controlled by activated diffusion.

Thus, the range *R*1 comprises only those molecules which are able to leave the pores relatively quickly due to either sitting close to the crystal surface or being not considerably hindered from diffusion as in the case of non-substituted $AlPO_4$-31 (Fig. 2a). Thereafter, within the range *R*2, the remaining template molecules and their fragments undergo further cracking along with simultaneous or subsequent burning out. A partial removal of the cracking products by desorption is also possible.

These considerations have been confirmed by mass spectroscopy analysis of the desorbed gases (Fig. 3). Within the range *R*2 (measurement period above 1.5 h), the prevailing masses are *m/z* (reduced molecular mass) equal to 18 (H_2O) and 44 (CO_2). In contrary, within the range *R*1 (measurement period about 1.3 h), further masses ($m/z = 54$ and higher) have been detected that represent fragments or, more likely, partially oxidized fragments of template. Di-*n*-propylamine itself ($m/z = 101$) was missing completely during the whole detemplating process. This is not in agreement with the interpretation of burning out of template from the likewise unidimensional pore systems of MgAPO-39 (pore diame-

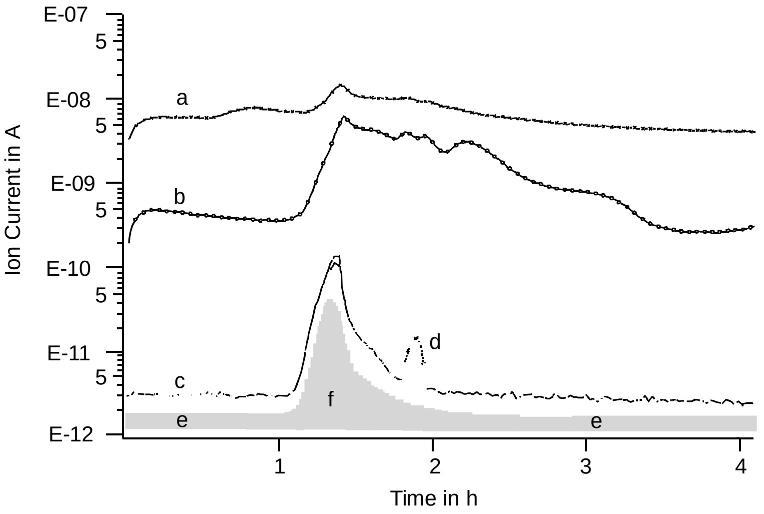

Fig. 3. Mass spectra of the products evolved from the sample no. 4 (MnAPO-31) measured with the method 2. Ion current (A) in dependence on time. *m/z* are equal to: (a) 18 (H_2O); (b) 44 (CO_2); (c) 54 (?); (d) 57 (?); (e) (≤1.1 h and ≥2 h) 56, 84 (?); (f) (1.1–2 h) 56, 58, 64, 70, 84, 96 (?) (intensities within (f) strongly scattering and partially overlapping).

ter 0.4 nm) and MgAPO-50 (0.7–0.8 nm) up to 579 [14] and 710 K [16], respectively, accepted as a release of water and unaffected di-*n*-propylamine. Only above these temperatures, the detemplation has been assumed to turn into combustion process. However, since none of the compounds set free has been confirmed analytically, the presumed calcination mechanisms fail to be evidenced. Then, it seems more justified to accept the processes running like those observed for the MeAPO-31 system studied.

ZnAPO-31, in comparison with Mn APO-31, showed the very same dependences with respect to the occurrence of the particular combustion compounds and to their relative intensities in the mass spectra (not shown since not offering further details).

Seemingly inconsistently with the marked formation of CO_2 and H_2O within the range $R1$, the desorption process is endothermic (Fig. 4a). Obviously, water has been occluded during the synthesis in the pores in such a way that it cannot exit before template starts to burn out. This endothermic setting free of water prevails all exothermic processes of template oxidation. Only within the range $R2$, the process turns exothermic and reaches maximum in line with the peak P2.

As compared with the original samples, the manually ground materials manifested significantly differing features of burning out (Fig. 4b). Enlarged surfaces and shortened pathways led to enhanced accessibility to oxygen and improved gas exchange. Features of desorption resemble in tendency those of non-doped $AlPO_4$-31: the range 2 decreased since burning partially occurred at lower temperatures. Its exothermic maximum appeared by about 200 K earlier and, consequently, the desorption peak P1 was almost not endothermic.

At about 400 K, a higher loss of mass was observed after grinding (Fig. 4b). It is to derive from the augmented adsorption of water on numerous additional hydrophilic terminal OH groups on the crushed surfaces of the crystallites.

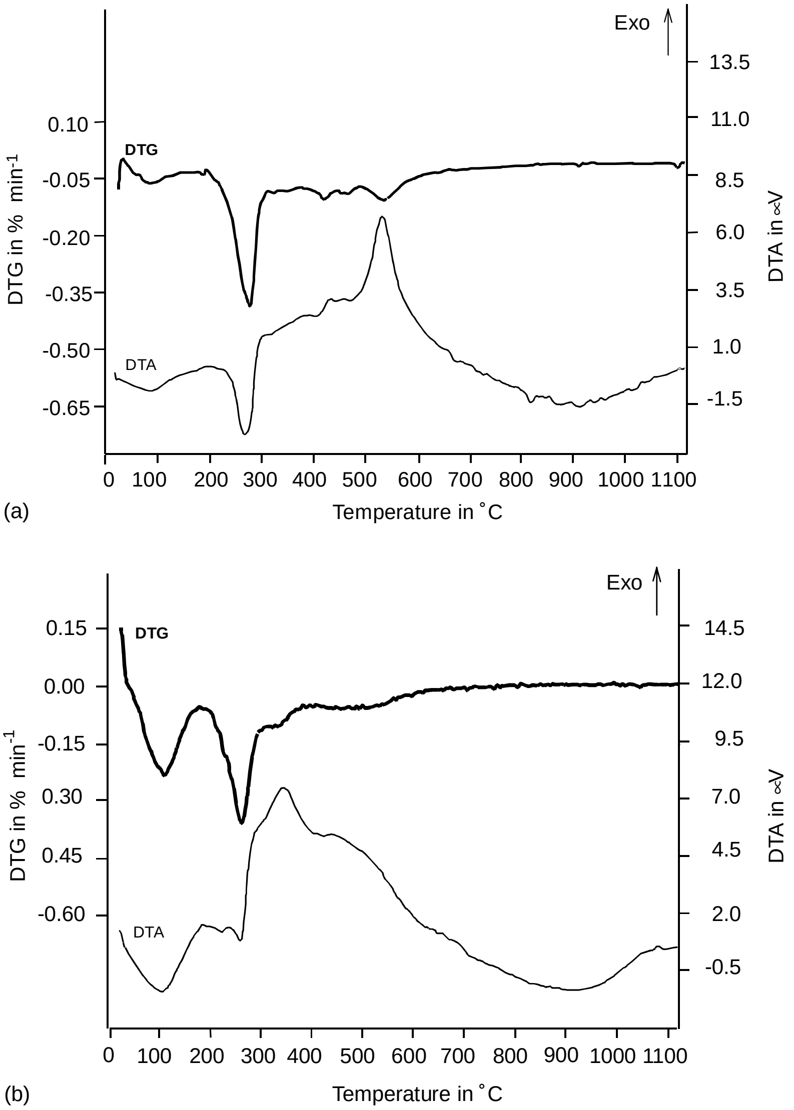

Fig. 4. DTG and DTA profiles of the sample no. 4 (MnAPO-31) measured with the method 2: (a) sample as prepared; (b) sample after manual grinding.

All samples undergo transition from the ATO structure into a denser aluminophosphate analogous to β-cristobalite as follows from temperature-programmed Guinier technique [8]. Temperature of structure break-down decreases with increase in the content of heteroatoms (Table 1, Fig. 1). It falls from above 1323 K for CuAPO-31 down to 1103 K for ZnAPO-31. If this tendency would be continued steadily, samples containing ca. 2.5 u.c./Me should collapse at about 750 K, i.e. already within the range of calcination. Corresponding temperature dependent tendencies have been reported for CoAPSO-44 [19] and for the MeAPO-16 system [27]. Most of the MeAPO-*n* materials reported in the literature contain considerably higher amounts of heteroatoms than those examined in this study. For such materials, an appropriate grinding might allow to avoid structure collapse since it requires milder calcination conditions, provided that the crystal dimensions fail to be essential for subsequent processes. Furthermore, it would be worth of study if the crystal dimensions can get adapted by systematically modified synthesis conditions [28] to optimized conditions for detemplating.

4. Conclusions

$AlPO_4$-31 is characterized by only one DTG peak for the template removal. In contrast, burning out of the template, di-*n*-propylamine, from the MeAPO-31 proceeds in two separate temperature regions. The share of each region to the total process is dependent on the content of heteroatoms. Grinding of the samples results in an improved exchange of atmosphere and gaseous products that favours burning out at lower temperatures. A study should be performed to find out if crystals of different dimensions, which could directly be grown under appropriate synthesis conditions, may possibly exhibit similar effects.

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