

THERMAL DECOMPOSITION OF TRIPROPYLAMINE AS A TEMPLATE IN MeAPO-5 MOLECULAR SIEVES

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The thermal decomposition of tripropylamine as a template occluded in the pores of MeAPO-5 aluminophosphate molecular sieves was investigated by means of TG, DTG and DTA. The effects of the incorporation of metal ions [Be, Mg, Ca, Ni, Fe(II), Fe(III) and Zn] in the crystal framework on the complete removal of template molecules and on the thermal stability of the samples were considered.

The MeAPO-5 molecular sieves are representatives of a new class of microporous aluminophosphate materials whose potential adsorptive and catalytic properties are of considerable interest [1-4]. MeAPO-5 molecular sieves have been examined particularly with a view to carrying out syntheses in the presence of suitable organic templates and incorporating Fe [3, 4, 6-9], Co [3, 10-12], Mg [3, 4, 12], Mn [3, 13] and Zn [3-5] ions in the crystal lattice. According to the present view, the isomorphous replacement of Al by bivalent metal ions M(II) generates a negatively charged framework and, after the decomposition of the template, also acid centres which are of considerable importance in modifying the carboniogenic catalytic activity of the materials. Some indications have been mentioned regarding the incorporation of M(II) in the microporous framework during synthesis. Other data have been presented concerning a certain amount of M(II) being in non-framework positions, thereby probably compensating the negative framework charge. In spite of the considerable interest in these problems in the literature, there have been no comparative studies on the effects of chemical substitution upon the decomposition of the organic template, a

step which necessarily precedes the employment of molecular sieve materials.

This paper reports results of an investigation of the thermochemical properties of MeAPO-5 [metal ions = Be, Mg, Ca, Ni, Fe(II), Fe(III) and Zn] synthesized with tripropylamine (Pr_3N) as a templating agent. The effects of substitution on the decomposition of the organic material and on the thermal stability of the obtained samples were investigated by means of simultaneous thermal analysis methods (TG-DTG-DTA). The removal of the template in MeAPO-5 was compared with that in $\text{AlPO}_4\text{-5}$, SAPO-5 and BAPO-5, also prepared with Pr_3N . This was done because it allowed conclusions regarding the active centres and the ratio of neutral and protonated Pr_3N molecules occluded in the molecular sieve channels in the different modifications.

Experimental

Synthesis and characterization of the samples

The samples were prepared as described in ref. [14], by heating to 473 K a mixture of reagents of the same molar composition, i.e. 2.0 Pr_3N : 0.4 MO : Al_2O_3 : P_2O_5 : 50 H_2O . With the exception of pseudo-boehmite (Condea), all raw materials, i.e. SiO_2 , 85% H_3PO_4 , H_3BO_3 , Pr_3N , FeCl_2 and the corresponding oxides, were obtained from Merck. The crystallization was conducted in teflon bottles placed in stainless steel autoclaves. The samples were then washed with distilled water till pH 7, dried at 373 K and rehydrated in a desiccator over saturated $\text{Ca}(\text{NO}_3)_2$ solution. The degree of crystallinity was determined by means of X-ray powder diffraction, with SAPO-5 as a standard [14].

The samples were also characterized by the following techniques: IR spectroscopy in the region 1400-400 cm^{-1} , using a Specord 75IR spectrophotometer and KBr pellets; scanning electron microscopy, using an SEM 515/D 806 Philips apparatus and elemental analyses [15] for determination of the carbon content. All samples but ZnAPO were found to be highly crystalline (70 to 100%) (Table 1). Apart from an amorphous product, no other phase admixtures were detected. In all cases, the same morphology of the prepared crystals was observed: spheroidal aggregates consisting of small platelets. The Pr_3N content in MeAPO (Table 1) varied between 6 and 8 wt%, which is an indication of the similar adsorption capacities of the synthesized materials as compared to that of $\text{AlPO}_4\text{-5}$. The considered data are

Table 1 Chemical composition, crystallinity and thermal stability

N	Sample*	Reactants for synthesis	Chemical analysis		Crystallinity, %	Cryst. phases** and impurities
			Pr ₃ N, wt. %	H ₂ O, wt. %		
1	AlPO ₄ -5	AlOOH	7.6	7.3	100	5
2	SAPO-5	SiO ₂	9.2	4.7	100	5
3	BAPO-5	H ₃ BO ₃	7.8	6.3	75	A+5
4	BeAPO-5	BeO	7.4	7.6	100	5
5	CaAPO-5	CaO	5.8	11.8	82	A+5+T
6	MgAPO-5	MgO	6.1	9.0	100	A+T (major)
7	NiAPO-5	NiO	7.5	8.9	75	A+5
8	FeAPO-5	Fe ₂ O ₃	5.6	6.5	75	5 (major)
9	FeAPO-5	FeCl ₂	7.4	5.3	70	5+A
10	ZnAPO-5	ZnO	6.6	9.2	60	C+T (major)

*MeAPO-% is acronym for microporous metal aluminophosphates and the suffix "5" denotes a specific structure type [1]

**after heating at 1273 K in the DTA experiment, 5 = AlPO₄-5; T = tridimite; C = cristobalite; A = amorphous

in agreement with literature data [3-5] and can be used indirectly in support of the incorporation of metal ions in the aluminophosphate lattice.

Thermal analysis

The combined TG-DTG-DTA thermal analysis was conducted on an MOM OD-103 instrument under the following conditions: sample size: 0.1 g; reference compound: α -alumina; sample holder: platinum microcrucibles; temperature range: 293-1273 K; heating rate: 10 deg·min⁻¹; thermocouple: Pt/PtRh; atmosphere: static air.

Results and discussion

The results obtained indicate that the removal of H₂O and of the organic template in the samples (Figs 1-3) takes place in several stages (I-IV). The DTA curves reveal the existence of four distinct temperature regions, i. e. 293-513 K (I), 513-653 K (II), 653-793 K (III), and 793-953 K (IV). These stages are typical of the thermal processes taking place and are observed with minor deviations for the majority of the examined samples (Table 2). MgAPO-5, Fe(II)APO-5 and ZnAPO-5 are exceptions and their thermochemical properties will be considered separately. A comparison of the DTA curves and the data from the elemental analyses regarding the amounts of Pr₃N in the samples (Table 1) allows a more accurate discussion of the observed thermal effects and decomposition processes. The weight losses recorded in temperature range I are due to endothermic processes of dehydration (293-423 K), followed by simultaneous removal of water and template (423-513 K). The absence of an exothermic effect is an indication that this is the desorption of weakly bonded Pr₃N molecules which are probably not included in the channels of the molecular sieve; it amounts to about 10-15 % of the total quantity of the template in the sample. The decomposition of the amine begins at about 513 K for most MeAPO. The DTA curves reveal clearly observable exothermic maxima at about 573, 673 and 813 K (Table 2), which correspond to complex reactions of oxidation and decomposition in ranges II to IV. The oxidative exothermic processes obviously predominate over the endothermic desorption and cracking processes. Calculations based on weight losses show that in the interval II to IV the amount of template included in the molecular sieve channels varies between 85 and 100% of the total amount of Pr₃N present in the samples. The comparatively high temperatures at which the complete removal of

Pr₃N degradation residues ends are worth noting. Those results are in very good agreement with the data reported by other investigators for the APO₄-5 [5, 16] and ZnAPO-5 [5] systems. We have also observed similar results, but to different degrees, depending on the crystalline structure, in the thermal analysis of silicoaluminophosphates of various types [17].

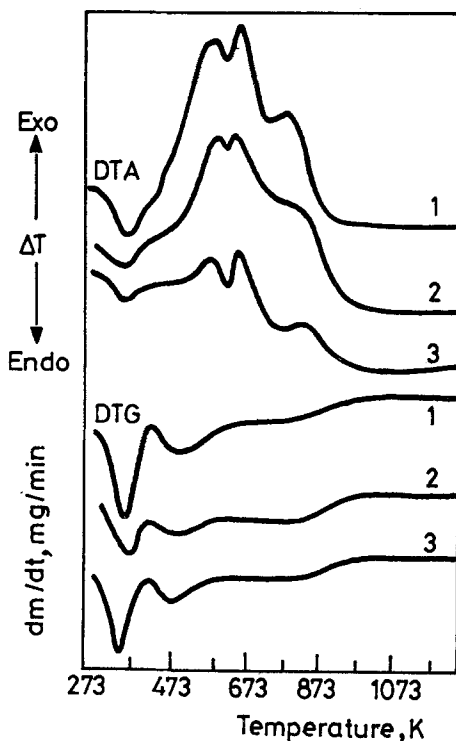


Fig. 1 DTG and DTA curves of: 1 - AlPO₄-5; 2 - SAPO-5; 3 - BAPO-5

After the elimination of the template ($T > 973$ K), other thermal effects are not observed in the DTA curves. This result does not completely exclude the loss of crystallinity or the formation of new phases taking place to a certain extent. Because of this, the samples heated to 1273 K were subjected to IR analysis for evaluation of their thermal stability. The degree of amorphization was determined from the decrease in intensity of the band at 560 cm^{-1} . The typical changes appearing in the intensities of the bands at

Table 2 Data on the DTA for the decomposition of the template

N	Sample	Temperature ranges of different stages, K				Initial temp. of template decomp., K	Temperature of exo-peaks, K
		I	II	III	IV		
1	AlPO ₄ -5	293-463	463-653	653-743	743- 923	463	603 683 803
2	SAPO-5	293-513	513-633	633-753	753- 973	513	613 633 813
3	BAPO-5	293-513	513-633	633-773	773- 973	473	573 663 833
4	BeAPO-5	293-513	513-653	653-793	793- 953	513	633 733 813
5	CaAPO-5	293-513	513-653	653-753	753- 933	513	573 673 813
6	MgAPO-5	293-513	-	693-833	833-1073	643	- 773 953
7	NiAPO-5	293-513	513-653	653-753	753- 933	513	583 663 803
8*	FeAPO-5	293-503	503-643	643-753	753- 933	503	583 673 813
9*	FeAPO-5	293-683	-	683-873	873- 973	683	- - 833
10	ZnAPO-5	293-553	553-693	693-823	823-1023	553	643 733 933

* - Samples are synthesized with Fe(III) and Fe(II), respectively

725 and 560 cm^{-1} and the formation of a new doublet at 733-712 cm^{-1} are indications of the appearance of tridimite and cristobalite, respectively.

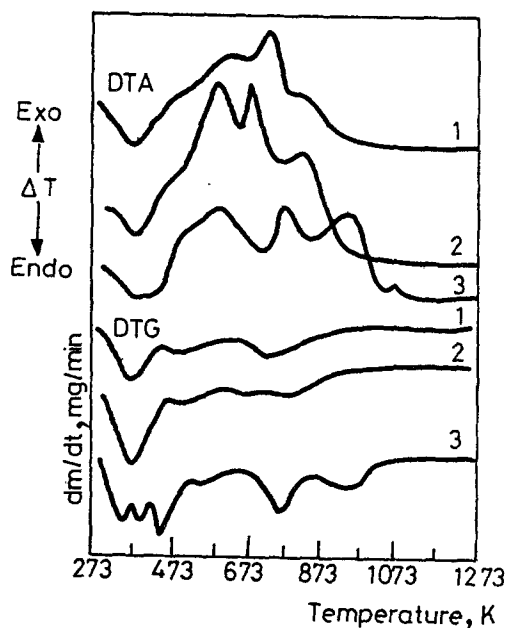


Fig. 2 DTG and DTA curves of: 1 - BeAPO-5; 2 - CaAPO-5; 3 - MgAPO-5

On the basis of their thermal behaviour, the samples can be arranged in the following three groups:

- 1) AlPO₄-5, SAPO-5 and BeAPO-5, in which the high crystallinity remains practically constant;
- 2) BAPO-5, CaAPO-5, NiAPO-5 and FeAPO-5, in which the partial formation of an amorphous phase takes place;
- 3) MgAPO-5 and ZnAPO-5, in which the crystal lattice is destroyed and tridimite and cristobalite are formed.

The results obtained concerning the thermal stability of ZnAPO-5 and the samples belonging in groups 1 and 2 are in good agreement with the data relating to the crystallinity of the initial samples. The poor thermal stability of MgAPO-5 is surprising, and may be connected with the decomposition of Pr₃N at considerably higher temperatures in this sample (see below).

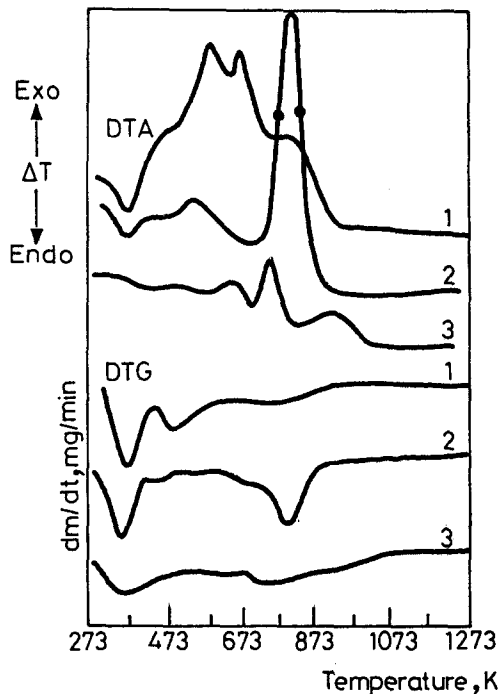


Fig. 3 DTG and DTA curves of: 1 - Fe(III)APO-5; 2 - Fe(II)APO-5; 3 - ZnAPO-5

According to the present view, the substitution of Si for P and M(II) for Al in the aluminophosphate lattice generates negative charges, which are compensated by the positively charged template. Therefore, in contrast with the electroneutral $\text{AlPO}_4\text{-5}$ framework, in the substituted forms neutral and protonated Pr_3N molecules are to be expected, the latter being decomposed at elevated temperatures. A similar shift in the temperature interval of organic cation decomposition has been observed with zeolites of ZSM-5 type [18], and also some substituted aluminophosphates [6, 19]. The results obtained (Table 2) indicate that all substituted forms have higher initial and final decomposition temperatures for Pr_3N as compared to $\text{AlPO}_4\text{-5}$. At the same time, the similar courses of the thermal curves for $\text{AlPO}_4\text{-5}$ and most of the samples modified with Si, B, Fe(III), Be, Ca and Ni can be interpreted in the neutral organic molecules predominate in the molecular sieve channels and act mainly as a space filler with weak van der Waals interactions [20]. This effect can be explained if it is assumed that the Si, B and Fe(III)-containing samples predominantly involve incorporation mechanisms that do not generate negative lattice charges. In the case of MeAPO (metal

ions = Be, Ca, Ni), compensation of the lattice charge by the non-framework metal cations can be expected to decrease the relative proportion of the protonated amine [2].

More specific results indicate that the DTA curves for Fe(II)APO-5, ZnAPO-5 and MgAPO-5 point to the existence of a more pronounced template lattice interaction as compared to the remaining samples. The decomposition of the organic material begins [Fe(II)- and MgAPO-5] and ends (Zn- and MgAPO-5) at significantly higher temperatures. Most notable is the shift for MgAPO-5, which is in agreement with the higher acidity and carboniogenic catalytic activity of Mg-containing samples [2, 21]. The highly intensive exothermic peak observed at 813 K for Fe(II)APO-5 is probably due to the simultaneous oxidation of Fe(II) to Fe(III) during calcination in air, which has also been reported by other authors [8].

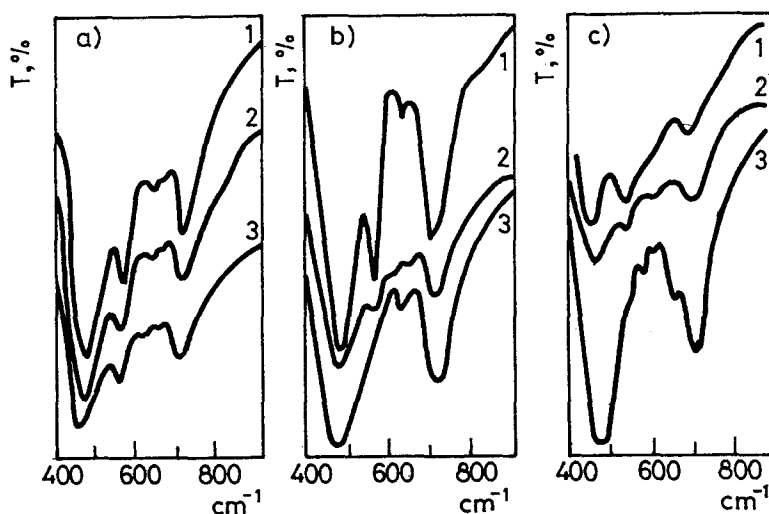


Fig. 4 IR-spectra of the samples heated to 1273 K a) 1 - AlPO₄-5; 2 - SAPO-5; 3 - BAPO-5; b) 1 - BeAPO-5; 2 - CaAPO-5; 3 - MgAPO-5; c) 1 - Fe(III)APO-5; 2 - Fe(II)APO-5; 3 - ZnAPO-5

Conclusions

The Mg, Zn and Fe(II)-containing samples exhibited the most pronounced differences regarding the decomposition of Pr₃N as compared

to $\text{AlPO}_4\text{-5}$. The effects are ascribed to a template-lattice interaction and to the oxidation of Fe(II) ions.

At the same time, the similar courses of the thermal curves for $\text{AlPO}_4\text{-5}$ and the samples modified with Be, Ca, Fe(III) and Ni indicate that the neutral organic molecules predominate in the channels of the molecular sieve. In the latter case, compensation of the negative lattice charge by the non-framework M(II) cations can be expected to decrease the proportion of the protonated amine.

The thermal stability of the crystal lattice of the substituted samples is lower than that of $\text{AlPO}_4\text{-5}$, BeAPO-5 being an exception. The lowest thermal stability is exhibited by the Mg and Zn-containing materials.

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Zusammenfassung — Mittels TG, DTG und DTA wurde die thermische Zersetzung von Tripropylamin, eingeschlossen in den Poren von MeAPO-5 Aluminophosphat-Molekularsieben untersucht. Es wurde weiterhin der Einfluß der Einlagerung von Metallionen [Be, Mg, Ca, Ni, Fe(II), Fe(III) und Zn] im Kristallgitter auf die vollkommene Abgabe der eingeschlossenen Moleküle und auf die thermische Stabilität der Proben untersucht.