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THERMAL DECOMPOSITION OF ORGANIC TEMPLATES IN SILICOALUMINOPHOSPHATE MOLECULAR SIEVES WITH VARIOUS STRUCTURES

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The decomposition of organic templates in molecular sieves SAPO-5, SAPO-11, SAPO-20, SAPO-34 and SAPO-37 was investigated by TG, DTG and DTA. In the case of SAPO-5, the decompositions of various organic templates were studied. The effects of the type of crystal structure, the pore size and the channel system on the complete removal of the organic material were considered.

The silicoaluminophosphate molecular sives, denoted SAPO-*n*, are new materials whose physical, chemical and catalytic properties have been the subject of considerable interest [1-7]. Microporous oxides SAPO-n can be considered to originate from Si incorporation into a hypothetical aluminium phosphate lattice. When Si substitutes one P, a negatively charged framework is formed and, after decomposition of the template, acid sites are also generated. These are of considerable importance in modifying the carboniogenic activity of these materials [1, 2]. In the presence of suitable organic templates, silicoaluminophosphates with different crystal structures have been synthesized [1, 8, 9].

This work continues our previous investigations on the removal of the templating agent from aluminophosphate-based molecular sieves, by means of simultaneous thermal analysis (TG-DTG-DTA) methods [10]. We now

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wish to compare the thermochemical properties of "as-synthesized" SAPO-5, SAPO-11, SAPO-20, SAPO-34, SAPO-37 and the zeolite ZSM-5 (Table 1), which differ considerably in crystal structure, pore size and channel system [11]. In the case of SAPO-5, the decompositions of various organic templates in one and the same structure have also been investigated. The obtained information is of importance as regards the choice of the right conditions for the thermal treatment of the molecular sieve precursors, since template removal is a necessary step prior to their use as adsorbents or catalysts. Comparative investigations of this type have not been carried out on SAPO-*n*. Studies on different microporous aluminophosphates $AlPO_4$-5 [12-14] and AlPO-11 [15] have shown that complete removal of the template molecule encounters considerable difficulties.

Experimental

Synthesis and characterization of the samples

The SAPO samples were prepared as described in Ref. 9 by heating a mixture of reagents, usually of the same molar composition i.e. $2R \cdot 0.4SiO_2 \cdot Al_2O_3 \cdot P_2O_5 \cdot 50H_2O$, in which R is the corresponding template molecule. With the exception of pseudoboehmite (Condea Chemie) and tetrapropylammonium hydroxide (TPAOH) (Alfa product), all raw materials and templates were obtained from Merck i.e. SiO_2, 85% H_3PO_4, tripropylamine (Pr_3N), triethylamine (Et_3N), N,N-diethylethanolamine (DEEA), di-*n*-propylamine (Pr_2NH), isopropylamine (iPr_2NH), tetraethylammonium hydroxide (TEAOH) and tetramethylammonium hydroxide pentahydrate ($TMAOH \cdot 5H_2O$).

Table 1 Structure of the samples

Sample*	Structure Type	Pore size, nm	Porosity	Channel system accord. to ref. 11
SAPO-5	$AlPO_4$-5	0.8	large	1 - dimensional
SAPO-11	$AlPO_4$-11	0.6	medium	1 - dimensional
SAPO-34	chabazite	0.43	small	3 - dimensional
SAPO-37	faujasite	0.8	large	3 - dimensional
SAPO-20	sodalite	0.3	very small	apertures formed by
ZSM-5	pentasil	0.6	medium	3 - dimensional

*SAPO-*n* is an acronim for microporous silicoaluminophosphates and the suffix "n" denotes a specific structure type [1]

The crystallization was performed in teflon bottles placed in stainless steel autoclaves. The samples were then washed with distilled water, dried at 373 K and rehydrated in a desiccator over saturated $Ca(NO_3)_2$ solution.

Table 2 Elemental analyses

Sample	Elemental analysis		Template* Volume, cm^3/g	
	Template, wt%	H_2O, wt%	This work	Ref. [4]
Pr_3N- SAPO-5	9.2	4.7	0.13	-
Et_3N- SAPO-5	9.2	3.6	0.13	0.16
DEEA- SAPO-5	17.1	7.7	0.19	-
TPAOH- SAPO-5	16.9	6.9	-	-
Pr_2NH- SAPO-11	7.2	3.1	0.10	0.11
iPrNH- SAPO-34	15.2	5.2	0.22	0.24
TMAOH- SAPO-20	14.8	4.7	-	-

*Calculated assuming liquid density for template [4]

The samples were characterized by the following techniques: X-ray powder diffraction patterns were measured with an Iso-Debyeflex 1000 Diffractometer [9]; the IR spectra (1400-400 cm^{-1}) were recorded with a Specord 75IR spectrophotometer, in KBr pellets; the scanning electron micrographs were taken with a Phillips instrument; the elemental analysis for determining the carbon content was conducted as reported in Ref. 16. The X-ray data indicated that all samples were highly crystalline. The results obtained for the template volumes (Table 2) and the lattice vibration spectra are in agreement with the literature data [3, 4, 17] and support the assumption of Si incorporation in the framework.

The ZSM-5 (SiO_2/Al_2O_3 200) sample was prepared in the presence of TPABr as already described [7].

Thermal analysis

The combined TG-DTG-DTA thermal analysis was conducted on a MOM OD103 apparatus under the following conditions: sample size 0.4 g; reference compound, α-alumina; sample holder, platinum polyplate type; temperature range, 293-1273 K; heating rate 10 $deg \cdot min^{-1}$; thermocouple, Pt/PtRh; atmosphere, flowing air. Some model samples obtained after mixing of dehydrated α-alumina with Pr_2NH, Pr_3N or TPAOH were also examined. In these cases, the evolution of the organic material takes place at about 433 K without an exothermic reaction.

Results and discussion

Template decomposition in SAPO-5

The results obtained with SAPO-5 (Figs 1 and 2) synthesized in the presence of different organic molecules indicate that removal of H_2O and the template preceeds in four stages (I-IV). The DTA curves reveal the following temperature intervals, which correspond to the initial and final temperatures of these stages: I 293-413 K, II 413-573 K, III 573-773 K and IV 773-973 K. Comparison of the DTG and DTA curves with the elemental analysis data (Table 2) demonstrates that the endothermic effects in ranges I and II are due to dehydration and the simultaneous removal of water and template, respectively. Calculation on the basis of the TG curves (Table 3) indicate that except for sample N4 about 28% of the total template amount is eliminated during stage II. The absence of an exothermic effect suggests that the organic molecules are most probably desorbed or destroyed without the participation of oxygen.

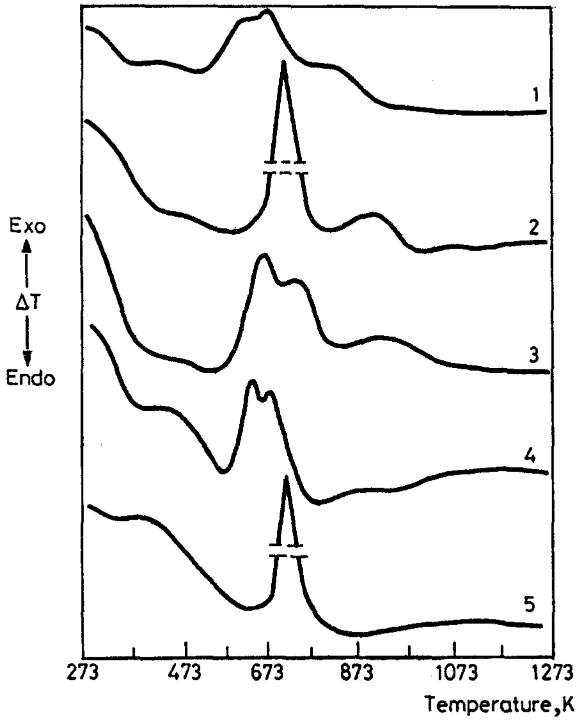

Fig. 1 DTA of SAPO-5 with different templates (curves 1-4) and TPA-ZSM-5 (curve 5): 1 - Pr_3N; 2 - Et_3N; 3 - DEEA; 4 - TPAOH

Treatment at higher temperatures (stage III) leads to intensive thermooxidative destruction of the occluded organic material and, in most cases, to the appearance of two exothermic effects. A considerable proportion of the template (40-44%) is eliminated in this interval.

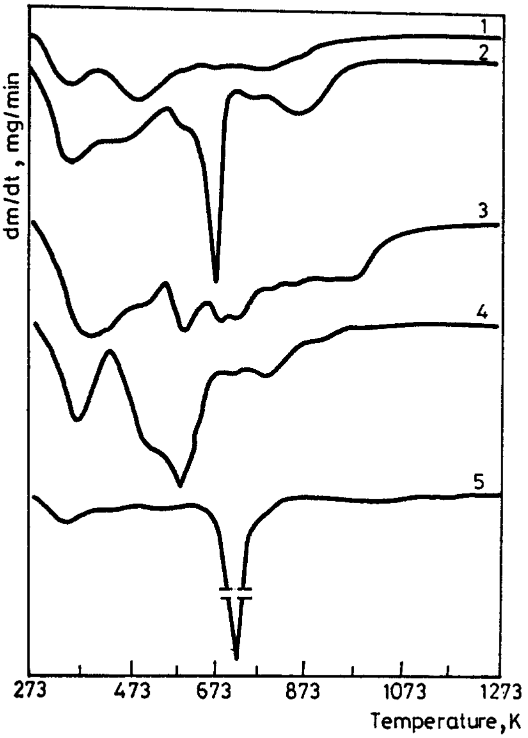

Fig. 2 DTG of SAPO-5 with different templates (curves 1-4) and TPA-ZSM-5 (curve 5):
1 - Pr_3N; 2 - Et_3N; 3 - DEEA; 4 - TPAOH

The removal of the template is completed in the next stage (IV). At the beginning of this interval, the samples are grey and further oxidation of carbonaceous residues produced by the template decomposition obviously takes place. These heavy products amount to 15-30% of the total organic material, and the corresponding thermal effects are weaker.

In addition to the general relationships, the DTA curves show specific effects, depending on the template nature. The decomposition takes place at higher temperatures for samples N2 and N3 than for N1 and N4. By analogy with ZSM-5 [18] and some aluminophosphates [15], this effect can be interpreted as an indication of a more pronounced template-lattice interaction.

In other words, acid sites of different strengths may be produced, depending on the nature and dimensions of the organic agent. The higher acidity and carboniogenic catalytic activity of Et_3N-SAPO-5 as compared with those of the remaining samples [19] are in agreement with this assumption.

Template decomposition in SAPO-n

The results obtained (Figs 3 and 4) verify the complex nature of the template decomposition in the molecular sieve channels. In comparison with SAPO-5, the exothermic maxima are shifted and, especially in the case of SAPO-20, the temperature intervals of the different stages are also considerably different (Table 3). The DTG curves reveal specific effects of the crystal structure, which permits the application of thermal analysis for identification of the various SAPO's. As shown previously [7], combined thermal analysis proved very useful in the phase purity control of $AlPO_4$-5 and SAPO-5, together with X-ray and IR spectroscopy.

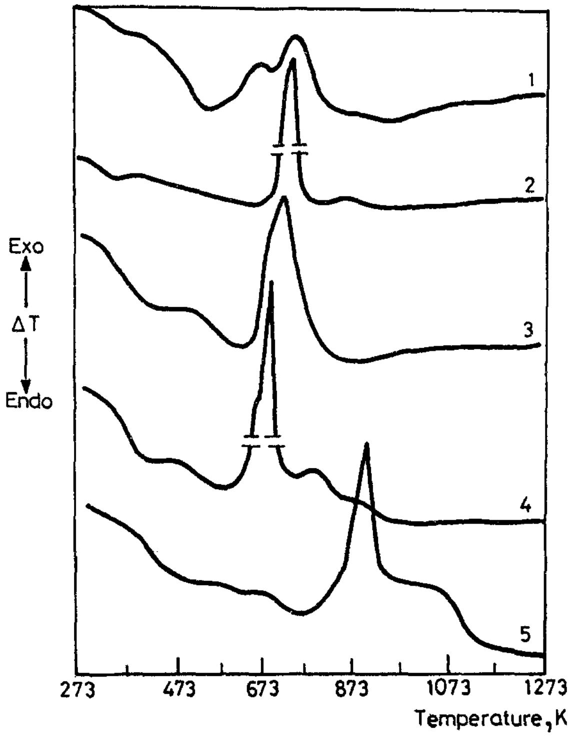

Fig. 3 DTA of SAPO-*n*: 1 - Pr_2NH-SAPO-11; 2 - $iPrNH_2$-SAPO-34; 3 - TEA-Pr_2NH-SAPO-34; 4 - TPA-TMA-SAPO-37; 5 - TMA-SAPO-20

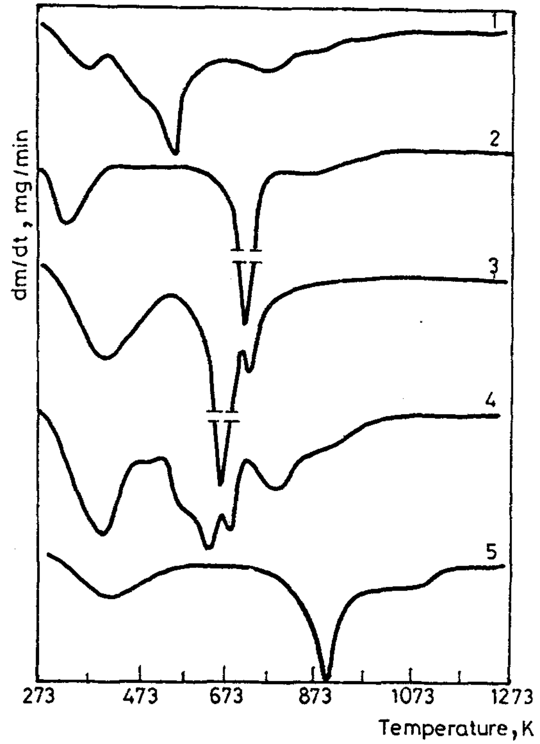

Fig. 4 DTG of SAPO-*n*: 1 - Pr_2NH-SAPO-11; 2 - $iPrNH_2$-SAPO-34; 3 - TEA-Pr_2NH-SAPO-34; 4 - TPA-TMA-SAPO-37; 5 - TMA-SAPO-20

Though templates of different chemical natures were used, the results of this study reveal to some extent the effect of the crystal structure on the decomposition of the organic material. A comparison of SAPO-*n* with SAPO-5 demonstrates the following characteristic particularities:

- the initial temperature of thermooxidative destruction (stage III) is higher by ca 50 deg;
- the proportion of the template removed by thermooxidative destruction is increased to 70% compared with 45%;
- the exothermic maxima are shifted towards higher temperatures in the range 673-773 K;
- the most considerable differences appear for SAPO-20; they will be considered separately.

These effects can be explained by taking into account the gradual decrease in pore size in the following sequence:

SAPO-5 > SAPO-11 > SAPO-34 > SAPO-20

Table 3 TG and DTA data for the template decomposition

N	Sample	TG data weight loss, %** Stages			DTA data Temperature of exo-peaks, K		
		II	III	IV			
1	Pr_3N-SAPO-5	28	44	28	623	673	833
2	Et_3N-SAPO-5	28	46	26	-	730	923
3	DEA-SAPO-5	24	48	28	653	753	923
4	TPA-SAPO-5	45	40	15	633	673	873
5	Pr_2NH-SAPO-11	22	45	33	643	773	-
6	i-$PrNH_2$-SAPO-34	25	65	10	-	723	-
7*	TEA-Pr_2NH-SAPO-34	14	72	14	-	743	-
8*	TPA-TMA-SAPO-37	20	69	11	703	793	913
9	TMA-SAPO-20	13	69	18	-	913	1023
10	TPA-ZSM-5	11	81	8	-	733	-

* The samples were synthesized using mixture of two templates

** Calculated as % of the total amount of the template

From one structure to another, the closeness of fit between the pore sizes and templates increases. The changes are most pronounced for SAPO-20, in which TMA ions are encapsulated within sodalite cages. This represents a considerable barrier to the diffusion of O_2 into and of decomposition products out of the channels. As a result of the transition from large to very small pores, the template decomposition requires a higher temperature.

Table 4 Content of carbonaceous residues after calcination*

Sample	Template	Carbon. residues, %**
SAPO-5	Et_3N	0
SAPO-5	DEAE	5.3
SAPO-11	Pr_2NH	3.4
SAPO -34	i-$PrNH_2$	6.8
SAPO-20	TMAOH	29

* The samples were calcined in air at the following conditions: gradual heating up to 873 K for 4 h and 2 h at 873 K in muffle oven;

** Calculated as a ratio of % of carbon before and after calcination

SAPO-37, whose pore size is the same as that of SAPO-5, is an exception from this relationship. The more difficult removal of TPAOH as compared to SAPO-5 may be explained by the stronger template-lattice interaction.

The effect of the dimensionality of the channel system can be discussed by comparing SAPO-5 and SAPO-11 with the other SAPO-*n*. The presence of 1-dimensional non-connecting channels favours the formation of carbonaceous residues, whose complete removal encounters considerable difficulties. The TG data support this assumption, by showing that the weight losses in stage IV increase from 8% (ZSM-5) to about 14% (SAPO-*n*) and 30% (SAPO-5 and SAPO-11) on moving from a 3- to a 1-dimensional channel system. The weight loss is the lowest in the case of ZSM-5, though it possesses considerably stronger acid sites than SAPO-5 [7] and SAPO-11 [6]. This result indicates that the more pronounced formation of heavy products in the samples with 1-dimensional channels is probably due more to the particular properties of the channel system than to the specific template-lattice interaction.

Conclusion

Except for SAPO-20, the thermooxidative decomposition of the organic material proceeds most intensively in the range 573(623)-773 K. There are considerable difficulties in the way of complete removal of the template from the SAPO's with a small porosity and a 1-dimensional channel system. A small proportion of the organic agent remains as carbonaceous residues, especially when the decomposition takes place in static air atmosphere (Table 4). In the case of SAPO-20, complete removal of the template is observed after destruction of the crystal structure.

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Zusammenfassung — Mittels TG, DTG und DTA wurde die Zersetzung von organischen Modelle in SAPO-5, SAPO-11, SAPO-20, SAPO-34 und SAPO-37 Molekularsieben untersucht. Im Falle von SAPO-5 wurde die Zersetzung verschiedener organischer Modelle untersucht. Weiterhin wurde auf den Einfluß von Kristallstruktur, Porengröße und Kanalsystem auf das vollständige Austragen des organischen Materiales eingegangen.