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THERMAL DECOMPOSITION OF CRYSTALLINE MOLECULAR SIEVE $(C_3H_7)_3N$–$AlPO_4$-5

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The thermal decomposition of $(C_3H_7)_3N$–$AlPO_4$-5 in inert and oxidizing gas atmospheres has been studied by TG, DTG and DTA in the temperature range 303–1273 K. The removal of tripropylamine occluded in the channels of the aluminophosphate occurs in a number of steps and is strongly influenced by the gas atmosphere.

$AlPO_4$-5 belongs to a novel class of crystalline micro-porous aluminophosphate phases (which are similar to zeolites in many properties), introduced recently by Wilson et al. [1, 2]. The crystal structure of this molecular sieve aluminophosphate has been well established [3]. It has a novel three-dimensional structure with hexagonal symmetry (cell constants: $a = 1.373$ nm, $c = 0.848$ nm and $\gamma = 120°$; unit cell composition: 12 $AlPO_4 \cdot nH_2O$) and contains one-dimensional channels (pore diameter = 0.8 nm) oriented parallel to the c-axis and bounded by 12-membered rings composed of alternating AlO_4 and PO_4 tetrahedra. $AlPO_4$-5 is synthesized in its TPA—OH (tetrapropylammonium hydroxide) and/or Pr_3N (tripropylamine) form and the organic template occluded in the channels is removed from the precursor crystals by heating in air at 673–873 K.

Thus, the thermal decomposition of Pr_3N–$AlPO_4$-5 is an important step for obtaining the aluminophosphate (with its channels free from the organic template) to be used as an adsorbent and catalyst and/or catalyst support.

Our earlier studies on the thermal decomposition of TPA–ZSM–5 indicated a very strong influence of the gas atmosphere on the decomposition [4] and also on the surface and catalytic properties of the resulting zeolite [5]. The present investigation was therefore undertaken with the objective of studying the thermal decomposition of Pr_3N–$AlPO_4$-5 under inert and oxidizing atmospheres with TG, DTG and DTA techniques.

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Experimental

Preparation and characterization of Pr_3N–$AlPO_4$-5

Pr_3N–$AlPO_4$-5 was synthesized according to the hydrothermal procedure outlined by Wilson et al. [6], by crystallizing it from a gel of composition 1.5 Pr_3N: 1.0 Al_2O_3: 1.0 P_2O_5: 40 H_2O at 423 K for 24 hr. The sources of the Al_2O_3 and P_2O_5 were bohmite (AlOOH) and ortho-phosphoric acid (BDH, AnalaR), respectively. The crystals of the aluminophosphate were washed thoroughly with deionized distilled water, filtered and dried in an air oven at 373 K for 16 hr.

The crystalline nature of the aluminophosphate was determined by means of X-ray powdered diffraction, using a Holland Philips PW/1730 X-ray generator with a Ni-filtered CuK_α radiation source and a scintillation counter. The XRD pattern for the aluminophosphate, shown in Fig. 1, is very similar to that of $AlPO_4$-5 reported earlier [2, 3]. No significant change in the XRD pattern of the aluminophosphate was observed when it was heated in air at 1273 K for 4 hr, indicating the high thermal stability of its structure.

The size and morphology of the crystals of the aluminophosphate were studied with a Cambridge Steroscan Model 150 Scanning Electron Microscope. The scanning electron micrographs of the aluminophosphate are shown in Fig. 2. The micrographs reveal that the aluminophosphate is well crystallized and the crystals have a distinctly hexagonal cross-section. The hexagonal rod-like crystals have a diameter of 12 ± 3 μm and a length of 20 ± 5 μm.

Carbon analysis on the aluminophosphate indicated that the concentration of tripropylamine occluded in the channels of the aluminophosphate is 9.1%. Hydrogen analysis indicated that, along with the tripropylamine, water molecules are also present in the channels of the aluminophosphate.

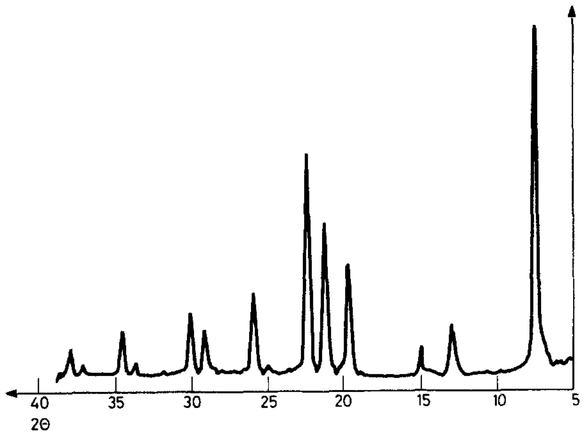

Fig. 1 XRD spectrum of the Pr_3N–$AlPO_4$-5

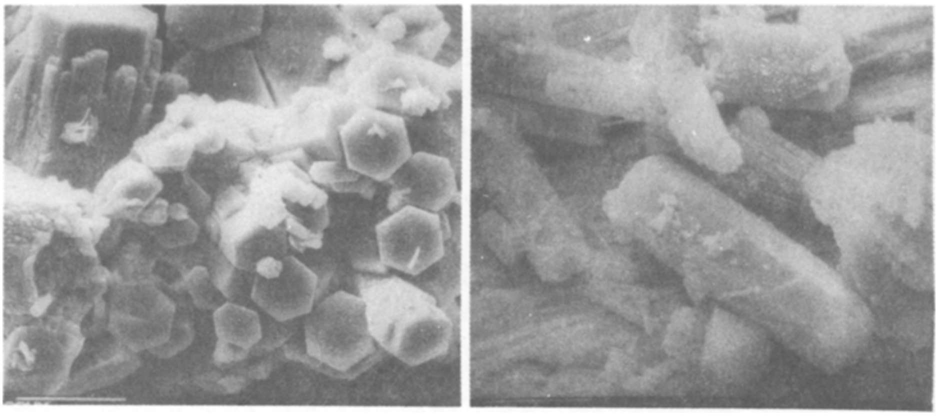

Fig. 2 Scanning electron microphotographs of the Pr_3N–$AlPO_4$-5

Chemical analysis showed that the Al/P (atomic) ratio for the aluminophosphate is 1.03.

Thermal analysis

Pr_3N–$AlPO_4$-5 dried at 373 K in air for 16 hr was used for the thermal analysis. The thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) data on the aluminophosphate were obtained under inert (in oxygen-free nitrogen) and oxidizing (in dry air) atmospheres, using an automatic thermal analyser (NETZSCH STA 409 Model) under the following experimental conditions: sample size, 25 mg; reference compound, α-alumina; sample holder, platinum crucible; temperature range, 303–1273 K; heating rate, 10 deg · min^{-1}; atmosphere, flowing air or nitrogen (flow rate: 100 ml · min^{-1}). The gases (N_2 and air) were of high purity (>99.99%) and were passed over activated 4A molecular sieves to remove traces of moisture.

Results and discussion

Thermal analysis of Pr_3N–$AlPO_4$-5 in inert atmosphere

The thermal curves (TG, DTG and DTA) for Pr_3N–$AlPO_4$-5 in an inert atmosphere are presented in Fig. 3.

The TG and DTG curves (Fig. 3) show that the removal of tripropylamine and water occluded in the channels of the aluminophosphate occurs in four distinct stages. The data on the temperature ranges and the weight losses for the different

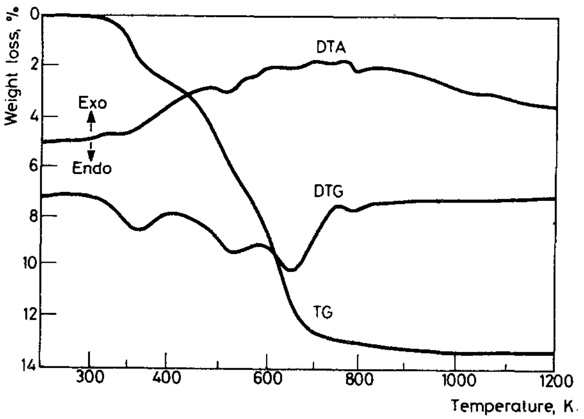

Fig. 3 TG, DTG and DTA curves for the decomposition of Pr_3N-$AlPO_4$-5 in nitrogen (Flow rate: 100 $cm^3 \cdot min^{-1}$)

stages are presented in Table 1. The data on the DTG ond DTA peak temperatures are given in Table 2. The results indicate that, in an inert atmosphere, all the processes occurring in the removal of the occluded material from the aluminophosphate are endothermic. The total weight loss in the decomposition is 13.45%. Since the concentration of tripropylamine in the aluminophosphate (estimated by carbon and nitrogen analysis) is 9.1%, the concentration of water in the aluminophosphate is expected to be 4.35%, part of which is adsorbed on the external surface, while part remains occluded in the channels of the aluminophosphate along with the tripropylamine.

The first stage is mostly due to the desorption of water adsorbed on the external surface and at the opening of the channels of the aluminophosphate. In the subsequent stages (at higher temperatures) the removal of tripropylamine and water occluded in between the molecules of tripropylamine is expected, mostly due to cracking of the occluded tripropylamine molecules to smaller fragments, which

Table 1 TG data of Pr_3N-$AlPO_4$-5 in different gas atmospheres

Stage of decomposition	N_2			Air		
	temp. range, K	wt. loss, %	total wt. loss, %	temp. range, K	wt. loss, %	total wt. loss, %
I	304–405	2.59	2.59	304–398	2.24	2.24
II	405–602	5.98	8.57	398–618	3.98	6.22
III	602–702	3.98	12.55	618–723	1.44	7.66
IV	702–985	0.90	13.45	723–922	4.47	12.13

Table 2 Data on DTG and DTA of Pr_3N–$AlPO_4$-5 in different gas atmospheres

Stage of decomposition	Peak temperature, K			
	DTG		DTA	
	N_2	air	N_2	air
I	350	350	343 (endo)	336 (endo)
II	525	524	513 (endo)	507 (endo)
III	645	676	660 (endo)	655 (exo)
			733 (endo)	—
IV	784	893	784 (endo)	879 (exo)

diffuse out from the channels of the aluminophosphate along with the occluded water molecules.

The cracking of tripropylamine is expected to occur as follows:

$$(C_3H_7)_3N \rightarrow 3\ C_3H_6 + NH_3 \qquad (1)$$

The cracking products have smaller molecular diameters (kinetic diameters of propylene and ammonia: 0.45 nm and 0.26 nm, respectively [7]) than that of tripropylamine (kinetic diameter about 0.80 nm); hence, these could easily diffuse out from the channels of the aluminophosphate. Since the channel diameter (0.8 nm) is very close to the kinetic diameter of the tripropylamine molecule, there is also a possibility of the direct removal of tripropylamine molecules by their diffusion from the aluminophosphate. The channels of $AlPO_4$-5 are polar [3] and therefore the tripropylamine molecules (which are also highly polar) are strongly held in the channels at lower temperatures. However, at higher temperatures, the desorption tripropylamine is expected to take place to an appreciable extent. Thus, in the overall removal of the tripropylamine molecules, the physical (desorption of tripropylamine) and chemical (the cracking of tripropylamine) processes occur simultaneously. The main removal of the tripropylamine occurs in stages II and III (Table 1).

The small weight loss (0.9%) in stage IV (temperature range: 702–985 K) is probably mainly due to the very slow desorption of ammonia and/or tripropylamine adsorbed strongly on the high-energy sites of the aluminophosphate. Our earlier study [8] on the temperature-programmed desorption of pyridine also indicated the presence of high-energy sites in $AlPO_4$-5; the site energy distribution in the aluminophosphate is rather broad. Thus, the removal of the occluded tripropylamine from the aluminophosphate in an inert atmosphere is a complex process occurring in multiple stages, resulting mostly because of the diffusion-controlled desorption of tripropylamine (the diffusion is expected to be an activated one) and the cracking of tripropylamine occurring simultaneously, and also because of the site energy distribution in the aluminophosphate.

Thermal analysis of Pr_3N–$AlPO_4$-5 in oxidizing atmosphere

The TG, DTG and DTA curves for Pr_3N–$AlPO_4$-5 in flowing air are presented in Fig. 4. In the oxidizing atmosphere too, the decomposition occurs in multiple stages. The temperature ranges and the TG data (weight loss) for the different stages are included in Table 1, and the corresponding DTG and DTA peak temperatures in Table 2.

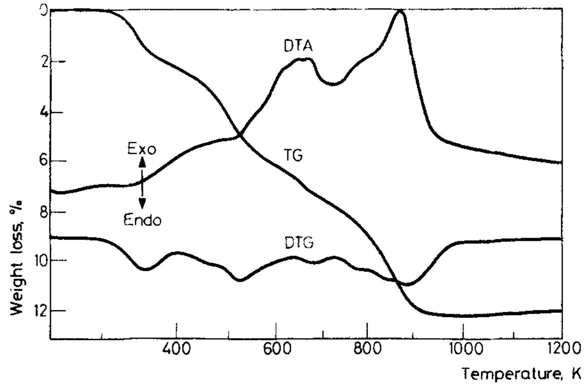

Fig. 4 TG, DTG and DTA curves for the decomposition of Pr_3N–$AlPO_4$-5 in air (Flow rate: 100 $cm^3 \cdot min^{-1}$)

The results show that the decomposition in the presence of air is a very complex process and occurs in four distinct stages (Fig. 3). The DTA data reveal that the processes occurring in the first two stages (i.e. stages I and II) are endothermic, whereas those occurring in the later two stages (i.e. stages III and IV) are exothermic. In the first stage, the desorption (an endothermic process) of water adsorbed on the external surface and at the opening of the channels of the Pr_3N–$AlPO_4$-5 occurs at the lower temperatures (304–398 K). In the second stage, the desorption of the occluded tripropylamine and water molecules and/or the cracking of the tripropylamine (also endothermic processes) are expected to take place. On the other hand, the removal of the tripropylamine in the last two stages is expected to be mostly due to its oxidative decomposition, which is an exothermic process. The natures of the TG, DTG and DTA curves (Fig. 3) show that the oxidative decomposition is a very complex process. It is expected to involve the thermal cracking of the occluded tripropylamine, followed by oxidation of the cracking products in the intra- and intercrystalline spaces, and also the direct oxidation of the tripropylamine within the channels. The oxidative decomposition within the channels is expected to occur mostly under oxygen-deficient conditions, because of diffusional limitations. This leads to the formation of heavy, complex oxygenates, which are difficult to remove from the channels because of their very low diffusivity. These oxygenates are removed by their further oxidation to simpler products (viz. CO_2 and H_2O), which can easily diffuse out from the channels. This is probably the reason for the delay in the removal of tripropylamine from the channels of $AlPO_4$-5 in the presence of air (up to 700 K, the extents of decomposition in N_2 and air are 93 and 60%, respectively).

Effect of gas atmosphere

A comparison of the results of the thermal analysis of Pr_3N–$AlPO_4$-5 in the inert and the oxidizing atmosphere (Figs 3 and 4 and Tables 1 and 2) shows that the thermal decomposition is very strongly influenced by the presence of oxygen. In both cases, the decomposition occurs in four distinct stages. In the presence of the inert atmosphere, the decomposition is endothermic in all stages. However, in the presence of the oxidizing atmosphere, it is endothermic in the first two stages and exothermic in the later two stages, thus involving the oxidative decomposition of tripropylamine at the higher temperatures. The total weight loss in the inert atmosphere is somewhat higher than that in the oxidizing atmosphere. The difference in the weight loss is mostly due to the change in the concentration of water in the aluminophosphate samples, resulting during their pretreatment. It is interesting, however, to note that, in the inert atmosphere, though complete decomposition occurs only at 985 K, about 93% of it has occurred up to 700 K. On the other hand, in the oxidizing atmosphere, the decomposition is completed at 922 K, but only 60% decomposition occurs up to 700 K. Thus, the decomposition is delayed in the presence of the oxidizing atmosphere. A similar observation has been made for the decomposition of TPA–ZSM–5 zeolites in inert and oxidizing atmospheres [4].

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Zusammenfassung — Die thermische Zersetzung von $(C_3H_7)_3N$-$AlPO_4$-5 wurde in inerter und oxydierender Gasatmosphäre mittels TG, DTG und DTA im Temperaturbereich von 303–1273 K untersucht. Der Austritt des in den Kanälen des Aluminiumphosphats okkludierten Tripropylamins erfolgt über eine Anzahl von Stufen und wird stark von der Gasatmosphäre beeinflußt.

Резюме — Методами ТГ, ДТГ и ДТА в инертной и окислительной атмозфере изучено термическое разложение $(C_3H_7)_3N$-$AlPO_4$-5 в интервале температур 303–1273 K. Выделение трипропиламина, окклюдированного в канальных пустотах решетки фосфата алюминия, происходит в несколько стадий и сильной зависит от газовой атмосферы.