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# Thermal behaviour of the largest known pore size molecular sieve VPI-5

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## Abstract

VPI-5 and $AlPO_4$-8 are crystalline aluminophosphate molecular sieves. An examination of the reported details on the synthesis of these materials revealed several common features suggesting the possibility of transforming the former to the latter by simple thermal treatment: this is confirmed by the thermogravimetric studies reported in the present work.

## INTRODUCTION

Virginia Polytechnic Institute-5 (VPI-5) is a molecular sieve aluminophosphate ($AlPO_4$) with the largest known pore size [1]. A recent paper by Davis et al. compares the physical properties of the molecular sieves VPI-5, $AlPO_4$-8 and $AlPO_4$-11 [2]. The details of the synthesis of $AlPO_4$-8, however, exist only in patent [3]; it is the least studied among the $AlPO_4$s and its structure has been only recently released [4]. Davis et al. [5] have reported the thermal treatment of VPI-5 without structural loss. Details of the procedure are unknown; evidently, calcination involves some unusual procedure.

## EXPERIMENTAL

We attempted to synthesise $AlPO_4$-8 following the procedure reported in the patent [3] using *n*-dibutylamine and *n*-dipentylamine as templating agents. Following this procedure, VPI-5 was the synthesis product! A re-examination of the patent literature revealed that $AlPO_4$-8 is described as ‘the major phase’ obtained by drying the as-synthesised product at 115 ° C. These and other considerations led to the identification of VPI-5 as a precursor to $AlPO_4$-8 [6] and the possibility that the former can be

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converted to the latter by thermal treatment. The present work reports the results of the thermal analysis of VPI-5.

VPI-5 was synthesised following the procedure of Grobet et al. [7] which eliminates the aging steps thought to be essential in the original procedure of Davis et al. [8]. *n*-Dibutylamine was used as the templating agent. Its identity was confirmed by XRD and NMR measurements.

Part of the sample of VPI-5 synthesised was used as such after air drying (sample 1). Another part was calcined at 500 ° C in a flow of dry air (20 ml $\text{min}^{-1}$) at a heating rate of 10 ° C $\text{min}^{-1}$ and then cooled (sample 2). A third part was dried at 115 ° C in air (sample 3). Samples 1 and 2 were stored over saturated ammonium nitrate solution in a desiccator at room temperature for 72 h before making the thermoanalytical measurements.

A Netzsch STA 409 differential thermal analyser was used to study the thermal behaviour of the samples. A description of the instrument and procedure followed are given elsewhere [9]. X-ray measurements were carried out in a Philips instrument using Cu K$\alpha$ radiation.

## RESULTS AND DISCUSSION

The thermoanalytical curves of samples 1 and 2 are shown in Figs. 1 and 2, and the data are presented in Table 1.

Both samples show weight loss up to 120 ° C corresponding to desorbed water. These are respectively 22% and 16%. In VPI-5, most of this desorbed water is known to be structural water [8]. This is reflected in the DTA endothermic peak maximum for VPI-5 which has a higher temperature (120–125 ° C) than that of sample 2 (90–95 ° C) obtained by its calcination and rehydration (Fig. 1). Desorption of water in either case is accompanied by the return of the octahedral aluminium (in the hydrated sample) to a tetrahedral co-ordination, as found in some $AlPO_4$ materials studied by NMR [6,10]. The lower percentage of desorbed water in the second case is consistent with the structural transformation reported which results in a reduced void space [11].

Weight loss above 125 ° C is negligible for both samples. This and the absence of an exothermic peak at high temperatures characteristic of the removal of occluded template, are in agreement with the reported role of the templating agent in the synthesis of VPI-5 [8].

Identical DTA curves for both samples above 125 ° C, with exothermic peaks at ≈ 280 ° C, suggest a common identity for the two samples above 125 ° C and that the probable transformation sample 1 → sample 2 takes place below this temperature, possibly at the drying temperature used by Wilson et al. [3] in the synthesis of $AlPO_4$-8. The exothermic peak at 280 ° C has to be attributed to some transformation that is common to both structures.

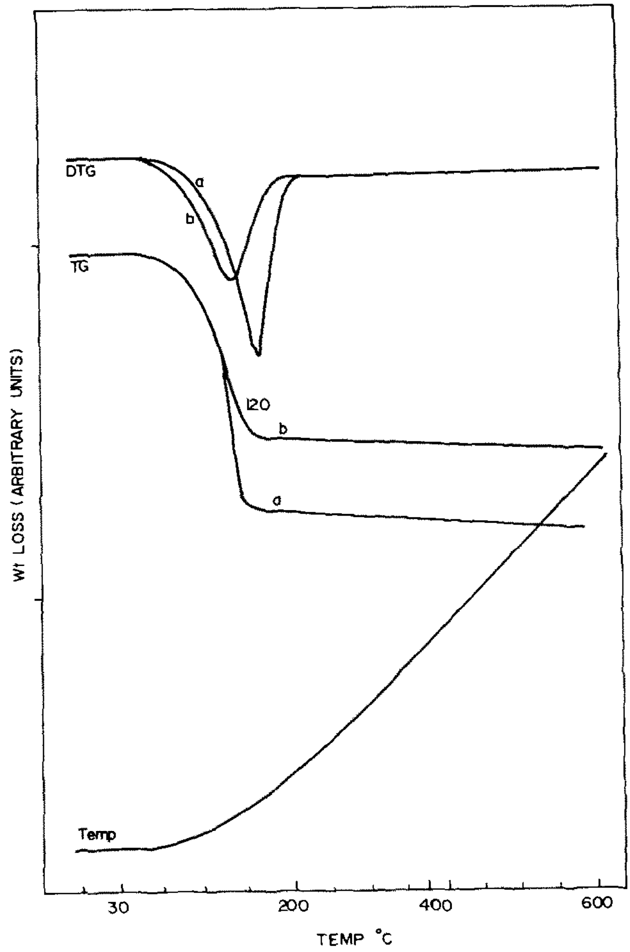

Fig. 1. TG and DTG traces of VPI-5 (curve a) and $AlPO_4$-8 (curve b).

Table 2 compares the XRD data ($2\theta$ values and the corresponding relative intensities, $I/I_0$, of the peaks) of VPI-5 (sample 1), VPI-5 dried at 115 °C and cooled to room temperature (sample 3) and $AlPO_4$-8 as reported in the patent [3]. The matching of these values demonstrates that the expected transformation has, indeed, taken place.

A recent paper by Vogt and Richardson [11] has described the reversible but partial transformation of VPI-5 to $AlPO_4$-8 at 77 ° C. The extent of the transformation has been studied using a high-temperature X-ray diffraction camera. This work provides further proof for the validity of our observations. However, we maintain that the transformation at high temperature is completely irreversible. Further, formation of the new structure by rearrangement of bonds does involve 'the first formation of VPI-5' [6]. This and the subsequent thermal treatment is represented in the scheme below in

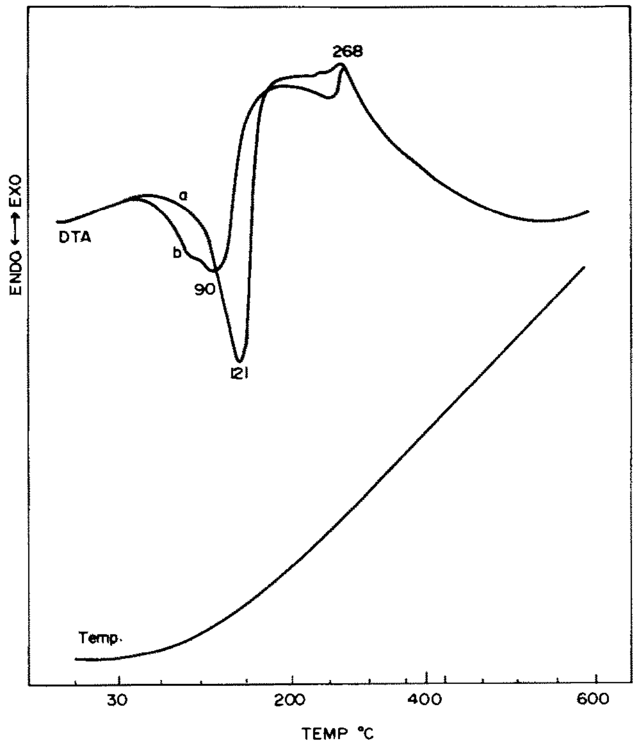

Fig. 2. DTA traces of VPI-5 (curve a) and $AlPO_4$-8 (curve b).

which DAA stands for *n*-dialkylamine, *n*-dipropyl to *n*-dipentyl, and TBAOH for tetrabutylammonium hydroxide.

$$n\text{-DAA/TBAOH} \cdot Al_2O_3 \cdot P_2O_5 \cdot 40H_2O \rightarrow \text{VPI-5}$$

$$\text{VPI-5} \underset{\text{dehydration}}{\overset{\text{low temperature}}{\rightleftharpoons}} AlPO_4\text{-8 (ref. 11)}$$

$$\text{VPI-5} \xrightarrow[\text{high temperature dehydration}]{\text{calcination or}} AlPO_4\text{-8}$$

TABLE 1

Thermal analysis data for samples 1 and 2

| Sample no. | Temp of DTG peak (°C) | Thermal nature of transformation | Temp range of DTA peak (°C) | Temp of DTA peak (°C) | Wt. loss (%) |
|---|---|---|---|---|---|
| 1 | 125 | Endo | 30–185 | 120 | 22 |
| | | Exo | 240–280 | 268 | – |
| 2 | 98 | Endo | 30–105 | 90 | 16 |
| | | Exo | 250–300 | 276 | – |

TABLE 2

X-ray powder diffraction data

| VPI-5 (as synthesised) | | VPI-5 (dried at 115 °C) | | $AlPO_4$-8 [a] | |
|---|---|---|---|---|---|
| $2\theta$ | $I/I_0$ (%) | $2\theta$ | $I/I_0$ (%) | $2\theta$ | $I/I_0$ (%) |
| 5.38 | 100.0 | 5.4 | 100.0 | 5.38 | 80.0 |
| 9.32 | 2.0 | 6.5 | 87.0 | 6.5 | 100.0 |
| 10.75 | 14.0 | 10.0 | 11.3 | 10.0 | 17.0 |
| 14.26 | 6.0 | 11.0 | 5.9 | 10.8 | 27.0 |
| 18.68 | 6.0 | 14.5 | 14.4 | 14.6 | 4.0 |
| 21.70 | 20.0 | 16.2 | 17.9 | 16.1 | 16.0 |
| 21.92 | 22.0 | 18.5 | 8.9 | 18.8 | 2.0 |
| 22.39 | 14.0 | 19.8 | 8.9 | 19.8 | 8.0 |
| 22.56 | 15.0 | 20.2 | 12.7 | 20.2 | 12.0 |
| 23.59 | 10.0 | 21.3 | 69.4 | 21.25 | 82.0 |
| 24.46 | 4.0 | 21.9 | 19.4 | 21.9 | 19.0 |
| 27.17 | 16.0 | 22.5 | 61.0 | 22.4 | 3.1 |
| 28.19 | 5.0 | 22.8 | sh | 22.7 | sh |
| 28.96 | 7.0 | 23.7 | 8.9 | 23.5 | 3.0 |
| 29.48 | 4.0 | 24.3 | 16.4 | 24.25 | 11.0 |
| 30.28 | 8.0 | 25.0 | 14.9 | 24.9 | 11.0 |
| 30.88 | 5.0 | 26.6 [b] | 7.4 | | |
| 32.71 | 7.0 | 27.4 | 4.4 | 27.1 | 2.0 |
| 35.86 | 3.0 | 28.2 | 4.4 | 28.2 | 5.0 |
| 38.32 | 3.0 | 29.2 [b] | 7.0 | | |

[a] Ref. 3.

[b] Impurity peaks.

## CONCLUSION

The largest pore size molecular sieve VPI-5 is a precursor to $AlPO_4$-8. Its transformation is straightforward but is not detectable by thermogravimetric measurements as it takes place during desorption of water from the aluminium phosphate hydrate [7].

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