Influence of washing and of heat-treatment conditions on the thermal stability of VPI-5

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Thorough washing of a VPI-5 synthesized with n-dipropylamine as template improves greatly its thermal stability while no major change is observed in the template content. A detailed study of the influence of the pretreatment conditions shows that in order to obtain a high thermal stability (up to at least 960 °C) two parameters are of importance. The removal of both the template and the adsorbed water requires either a low heating rate at atmospheric pressure or a low pressure (less than 3 Torr) when the heating rate is 300 ° per hour.

Keywords: VPI-5; stability; molecular sieve; post-synthesis treatments

1. Introduction

The synthesis of wide pore 18-ring aluminium phosphates were explored using several amines as templates. Systems studied in more detail involve the use of tetrabutylammonium hydroxide (TBAOH) [1–3] or a combination of triisopropanolamine and tetramethylammonium hydroxide [4]. They have been shown to be thermally and hydrothermally stable when thoroughly dehydrated under vacuum before heating [3,5]. Heating in conditions which do not consider in detail this parameter may transform VPI-5 structure into $AlPO_4$-8 for any template-form [6–10]. The samples prepared with n-dipropylamine (DPA) as template are said to be the least thermally stable forms [5] and not stable in the mother liquor [1]. This last result is not found by other researchers in Europe who found that DPA is a good template to obtain easily VPI-5 [11–13], better for instance than the tetrabutylammonium hydroxide (TBAOH) [11,12]. The present paper is devoted to a study of the thermal stability of VPI-5 synthesized with DPA with regards to the influence of washing and of the vapor pressure during heating.

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2. Experimental

MATERIAL

VPI-5 is synthesized as described in [1] using pseudoboehmite (Catapal B-alumina, Vista Chem. Co.), 85 wt% H_3PO_4 (Aldrich), and n-dipropylamine 99% (Aldrich). Similar results were obtained using n-dipropylamine gold label (99% +) purchased from Aldrich. After separation from the mother liquor the sample is washed by adding 200 ml of distilled water to about 18 g of VPI-5, stirring for 15 min and centrifugating the mixture. A first part of the batch is washed 5 times this way, the second part 15 times. The two parts are referred to as VPI-5A and VPI-5B respectively. Five different batches were prepared using DPA 99%. Attempts made to prepare VPI-5 with aqueous (55–60 wt%) tetrabutylammonium hydroxide as template obtained from Fluka were unsuccessful which is in line with what was observed in another laboratory using the same TBAOH source [11].

THERMAL TREATMENT

A weight of 0.5 g is heated in a U tube on a fritted glass under a flow of dry argon (10 l/hr) up to various temperatures.

TPD

A sample of 0.1 g of VPI-5 is placed in a U tube on a fritted quartz disc. It is pretreated at room temperature for at least 3 hr under vacuum ($< 10^{-3}$ Torr). The thermodesorption is carried out at a rate of 5° per min. The gas evolved is analyzed by a quadrupole mass spectrometer Quadruvac PGA 100 Leybold-Heraeus.

XRD

The X-ray diffractograms are recorded with a Siemens D500 diffractometer using the Cu K_α radiation. All the XRD studies are performed on samples rehydrated at ambient conditions.

3. Results and discussion

A. INFLUENCE OF WASHING

Table 1 gives the chemical analysis of samples VPI-5A and VPI-5B issued from the same parent batch. The C/N weight ratio is close to 5 i.e. to that of

Table 1
Chemical analysis (wt%)

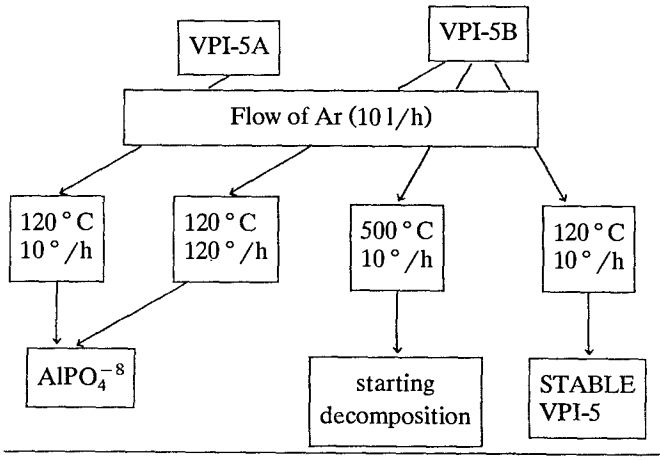
	C	N	Al	P	L.I [a]
VPI-5A	0.75	0.14	17.4	19.35	26.8
VPI-5B	0.70	0.13	17.05	18.5	23.5

[a] Loss on ignition at 1000 ° C.

n-dipropylamine. A first remark is that no significant difference in the results is observed for the differently washed solids. Within the accuracy of the analysis the same amount of DPA is present in both samples i.e. about 1 wt% which is slightly higher than the values reported for other VPI-5's (below 0.5 wt% for a mixture of template [4] or about 0.1 wt% for a DPA-VPI-5 [11]). In the present case this corresponds to approximatively 10^{-2} moles of DPA for 1.2 moles of water (or 5% in volume of DPA and 95% of water) in the materials as calculated from the loss on ignition at 1000 ° C. This amount of DPA which corresponds to an average of 0.3 molecule of amine per unit cell is similar to the value of 0.4 given in [13]. The question arises as to whether this small amount is enough to disturb the triple helix of water which is shown to be a part of the DPA-VPI-5 structure [13] and how washing which does not decrease the DPA content may affect the behaviour of VPI-5 upon dehydration. A first step is to consider the water removal.

Table 2 summarizes the influence of washing on the stability upon heating in an Ar flow at various rates. Fig. 1 gives the XRD patterns of the corresponding samples. VPI-5A washed only 5 times gives a mixture of VPI-5 and of $AlPO_4$-8 (fig. 1b) after heating up to 120 ° C at a rate as low as 10 °/hr. A similar partial

Table 2
Products resulting of VPI-5 heating depending on the heating conditions for VPI-5A (washed 5 times) and VPI-5B (washed 15 times)



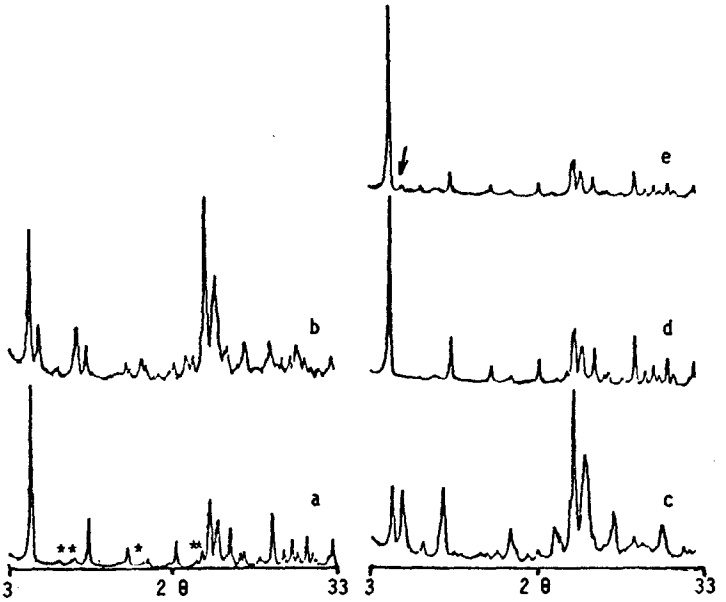


Fig. 1. XRD patterns of a: as-synthesized VPI-5, b: VPI-5A washed 5 times and heated at 120 ° (10 ° /h), c: sample VPI-5B washed 15 times and heated at 120 ° C (120 ° /hr), d: heated at 120 ° C (10 ° /hr), e: heated at 500 ° C (10 ° /hr). (*: impurities, arrow: beginning of decomposition).

transformation to $AlPO_4$-8 (fig. 1c) is obtained when the thoroughly washed VPI-5B sample is heated at the same 120 ° C temperature at a high heating rate (120 ° /hr). From VPI-5B the lower heating rate of 10 ° /hr leads to a stable VPI-5 material in the hydrated form at room temperature. The XRD pattern of this sample (fig. 1d) is similar to that of the as synthetized material (fig. 1a). Heating up to 500 ° C (10 ° /hr) of the sample VPI-5B gives a grey color and a XRD pattern (fig. 1e) which shows a new reflection at $d = 13.6$ Å in addition to all the reflections of VPI-5 structure seen in fig. 1a. This new reflection might suggest the beginning of a decomposition of the material. Several weak peaks (fig. 1a) seen in the starting sample and assigned to impurities are not detectable after the 500 ° C treatment (fig. 1e).

The grey color of the material VPI-5B after the treatment at 500 ° C suggests that the organic template might be decomposed to some coke trapped into the channels. In order to check the decomposition of the n-dipropylamine, TPD experiments were conducted at a rate of 300 ° /hr on the samples previously evacuated at room temperature in the TPD cell for 3 hr in order to evacuate a large part of physically adsorbed water. Fig. 2 gives the TPD spectra for the two samples A and B. A first remark is that the two materials give very similar TPD results. This is in line with the constant DPA content in both solids. Secondly in the dynamic conditions used, the template is fully decomposed above 500–600 ° C. The curves of fig. 2 related to the fragmentary ions issued from NH_3, H_2O, ethylene, ethane and propene show two steps in the decomposition, one

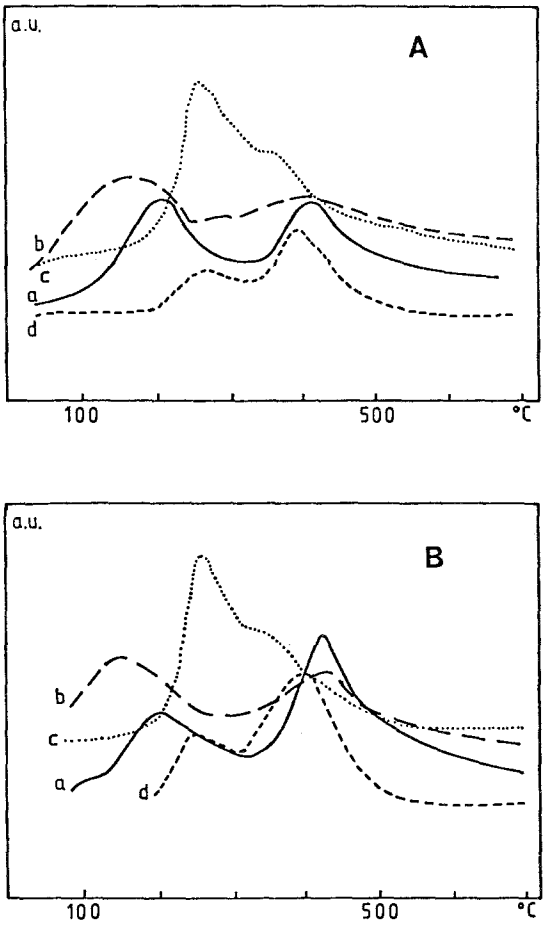


Fig. 2. TPD of samples VPI-5A (A) and VPI-5B (B). Heating rate 300 °/hr, pressure less than 10^{-3} Torr. a: mass 16 (NH_2^+), b: mass 18 (H_2O^+), c: mass 28 ($C_2H_4^+$), d: mass 42 ($C_3H_6^+$).

around 150–250 °C and the second one near 350–450 °C which might correspond to two different locations of the template.

The results above indicate that washing does not modify significantly the template decomposition but improves readily the stability of VPI-5 during heating. In addition a thorough washing makes the VPI-5B less sensitive to the rate of heating at 10 °C/hr up to 120 °C. The influence of washing is in line with what was briefly mentioned in the previous studies of VPI-5 [5,14]. This might be related not really to the removal of a small amount of template and its replacement by water but rather to a rearrangement of the template and water molecules in the channel favored in a pure aqueous medium leading to the formation of a more ordered triple helix of water as the one described in [13]. The washing water might, for instance, remove traces of alkaline ions which were introduced with the reactants during synthesis.

B. INFLUENCE OF A REDUCED PRESSURE DURING HEATING

Treatment of VPI-5A or VPI-5B under vacuum ($P < 10^{-3}$ Torr) at a heating rate of 300 °/hr was conducted as described in fig. 2. Several experiments were carried out up to 700 °C or 960 °C. After cooling down to room temperature under vacuum the samples were rehydrated in ambient conditions. Fig. 3a gives the XRD patterns of sample VPI-5B after heating at 960 °. It is similar to the one of the as synthesized sample or to the one of the sample heated only at 700 °C. The extra-reflections, which in fig. 1a were assigned to impurities disappear after heating. Both samples A and B give identical results and both are grey after the treatment indicating the presence of a small amount of coke. These experiments show that the influence of washing is less drastic when heating is conducted under vacuum.

In an attempt to reduce the coke content an experiment was conducted by heating sample VPI-5B at a rate of 300 °/hr in a flow (0.1 l/hr) of a He-O_2 mixture (ratio of flow rates $He/O_2 = 3$) at a pressure of 3 Torr and up to 700 °C. The material is white in contrast with the one obtained above under vacuum. After cooling down to room temperature and rehydration in ambient conditions the XRD pattern (fig. 3b) shows again a very good VPI-5 crystallinity with the disappearance of impurities shown in fig. 1.

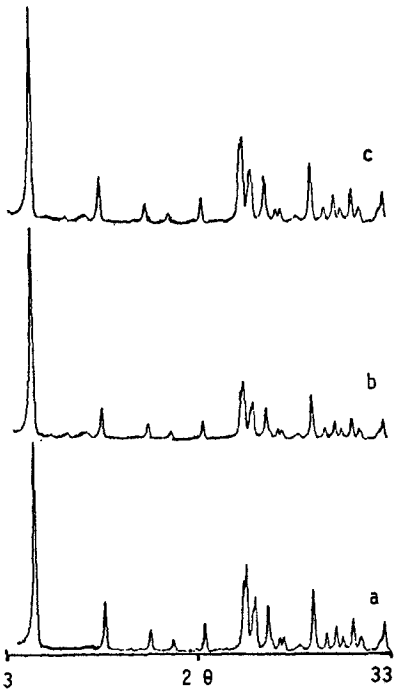


Fig. 3. XRD patterns of sample VPI-5B after a: heating at 960 °C under vacuum, b: after heating at 700 °C in a flow He/O_2, c: sample VPI-5A after heating at 700 °C under vacuum, rehydration at ambient conditions and evacuated at 120 °C and heated in air at 700 °C.

The integrity of the structure of VPI-5 obtained after decomposition of n-dipropylamine in the presence of O_2 is maintained. This suggests to remove first the major part of water by heating at 120° under vacuum at a heating rate of 100°/hr before any DPA decomposition. Then air is introduced in the line and the treatment goes up to 700°C at a heating rate of 300°/hr in order to decompose the template. The sample is transformed into $AlPO_4$-8. This experiment compared to the two previous ones shows that the template has to be decomposed under a reduced pressure in order to maintain the VPI-5 structure when the heating rate is 300°/hr. The five different batches of VPI-5 prepared behave similarly when heating under reduced pressure. All of them give TPD spectra similar to those of fig. 2 and highly crystalline VPI-5 after heating at 700°C.

C. INFLUENCE OF FURTHER HEATING AFTER REHYDRATION

The VPI-5B solids previously heated under vacuum (fig. 3a) or under oxygen (fig. 3b) are free of template. After the rehydration of such materials the question arises of their stability when only water is present in the channels. After heating of these rehydrated solids in air at a rate of 300°/hr both materials are transformed into $AlPO_4$-8. This indicates that a fast removal of water from the channels destroys the VPI-5 structure. In another approach, the sample VPI-5A was pretreated in vacuum up to 700°C as in TPD experiments (fig. 2A). As said previously the VPI-5 structure is maintained. After rehydration a TPD showed that only water is present in the channels. After a further rehydration of the same sample, it was evacuated (P less than 10^{-3} Torr) up to 120°C at a rate of 100°/hr in order to remove the larger part of water. The rate was then increased to 300°/hr and the treatment was performed up to 700°C in air. The sample is stable and only the VPI-5 phase is obtained (fig. 3c). This experiment demonstrates that after removal of a large amount of water during the evacuation up to 120°C the molecular sieve can withstand a fast heating (300°/hr) in air. This is in contrast to the experiment described in part B where a similar treatment applied to VPI-5 which still contains the template transformed the material into $AlPO_4$-8.

D. GENERAL COMMENTS

The VPI-5 prepared with n-dipropylamine as a template was described as the least stable materials in the VPI-5 family [5]. The present study shows that even in this case proper treatment conditions may lead to VPI-5 structure stable up to at least 960°C. It should be emphasized that the synthesis of VPI-5 using n-dipropylamine (99%) purchased from Fluka leads also to stable VPI-5 after careful dehydration [11]. The origin of the templates (for instance the alkaline ions impurities it contains) may induce different stabilities either during synthe-

sis as mentioned above for TBAOH or during heating as suggested here for DPA. The present experiments indicate that the removal of both water and template have to be carried out either at low heating rate at atmospheric pressure or at low pressure in order to avoid the transformation into $AlPO_4$-8. This may be related to the kinetics of water or template removal or/and, for water, to its presence in the liquid form above around 100 ° C in the channels. In SAPO-37 the existence of liquid water at temperatures lower than around 75 ° C was observed to destroy the crystallinity of the solid [15]. A reaction of liquid water with Al-O-P bonds was suggested. This may also be the case for VPI-5 as suggested in [5]. The stability of SAPO-37 and VPI-5, in presence of water, in different ranges of temperature may well arise from different energies of T-O bonds, themselves related to different bond angles and bond lengths in the two structures. In the present case no sign of reversibility of $AlPO_4$-8 to VPI-5 was observed in agreement with [5].

In conclusion DPA-VPI-5 structure may be maintained intact after heating up to at least 960 ° C.

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