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Use of sample controlled thermal analysis to liberate the micropores of aluminophosphate $AlPO_4$-11: evidence of template evaporation

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The thermal treatment of dipropylamine template occluded within $AlPO_4$-11 was studied using sample controlled thermal analysis under a residual pressure of 5×10^{-3} mbar. Intermediate samples, treated to different temperatures, were studied using FTIR and nitrogen adsorption manometry at 77 K.

The thermal treatment occurs in four steps. The first step (25 °C to 140 °C) corresponds to the dehydration of the hydrated dipropylamine. The second (140 °C to 210 °C) and third (210 °C to 330 °C) steps correspond to the main loss of whole dipropylamine molecules without degradation. A temperature induced evaporation type process would explain such a phenomenon. The final step (330 °C to 470 °C) corresponds to the degradation of a very small amount of dipropylamine in strong interaction with the $AlPO_4$ framework. The microporosity only becomes available to nitrogen adsorption during this final step.

Introduction

Aluminophosphate (or AlPO) zeotype materials arouse interest due to the possibility to synthesise well-defined pore structures with globally, electrically neutral frameworks. Potential uses of such materials are found in separation and encapsulation processes.

From a fundamental point of view, the interest in such materials lies in the lack of compensation cations within the pores. It is thus possible to investigate in detail adsorption processes within well-defined, neutral pores devoid of any cationic species.

The problem, however, for such fine adsorption studies, is to obtain samples with a minimum amount of defects to be able to render negligible any parasitic adsorption effects. Defects may arise from the synthesis proper, but more often, it is during the elimination of template molecules that the majority of defect structure is created. This step can lead to the extraction of heteroatoms (Al or P) or the formation of cracks within the crystals. Cracks may give rise, not only to parasite adsorption phenomena,[1] but also to a bypassing of compounds during membrane based separation processes.[2] The defects that occur during the thermal extraction of the template result from the considerable build up of pressure gradients within the pores. This arises from the blockage of degradation species formed that are unable to leave due to congestion at the entrances. The most common calcination protocols use linear heating ramps (around 1 K min^{-1}) up to a final temperature plateau that can be maintained for several hours. This can be carried out under nitrogen, oxygen or mixed N_2/O_2 atmospheres.

The drawback of such protocols is that it by no means takes into account the actual degradation reactions within the pores. This can lead to an overlap of different reactions, side reactions as well as a large increase in local pressure gradients within the pores. It would thus seem interesting to use a thermal calcination treatment that can be adapted to the sample, on-line, to the rate of reaction advancement under investigation.

Such a thermal treatment protocol has been developed in several laboratories and is given the general term "Sample Controlled Thermal Analysis" (SCTA).[3] Here feedback directly related to the rate of thermal transformation (*e.g.* rate of mass loss) is followed continuously and the sample is heated (or cooled) to control this transformation (*e.g.* constant rate of mass loss with time). Various different types of apparatus have been developed to work under vacuum or under different atmospheres. This technique has been used to follow numerous reactions (for example those noted in references 4 and 5), however few studies have used this technique to follow template elimination from zeolites[6] or related materials.[7,8]

An advantage in using such a technique over using a linear heating rate in the case of template elimination from zeolites is in the understanding of the mechanisms of degradation of the organic species. Indeed, SCTA methods allow the possibility to control the thermal treatment such as to separate various reaction steps that occur within a small temperature domain. The reproducibility attained allows the possibility to prepare samples with the "same thermal history"[4] up to various intermediate points in the transformation. It is thus possible either to analyse *in-situ* the decomposition products, or *ex-situ* the state of the sample at different points of the transformation. The knowledge of the reactions and side reactions can thus be transposed, allowing modification of more traditional heating protocols.

In the present study, the thermal degradation of dipropylamine from within the micropores of $AlPO_4$-11 has been investigated using SCTA. The initial aim was to control this reaction with time, allowing a characterisation of the different reaction steps. We chose the $AlPO_4$-11/dipropylamine system for this study as the amine species is linear, in contrast to many amine templates: (*e.g.* tetrapropylamine/ZSM5 and triethylamine/$AlPO_4$-5). The possibility therefore exists to wash out the template from the pores or extract the template under vacuum. We tried this latter procedure without success. An explanation may come from the unidirectional pores of relatively small pore aperture (0.39×0.63 nm^2) which severely limits the possibility of diffusion of the template species.

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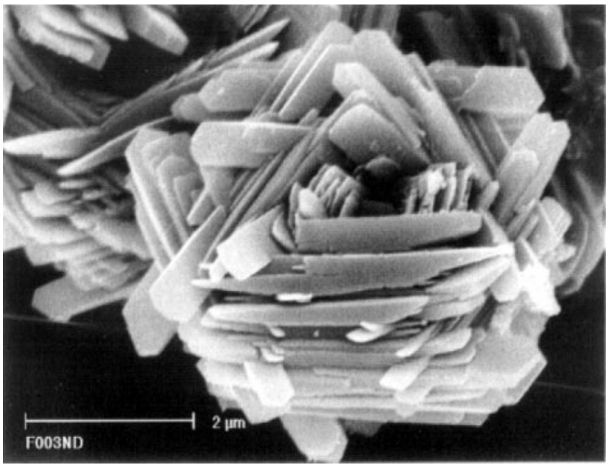

Fig. 1 SEM of the $AlPO_4$-11 sample used in the present study.

Experimental

Synthesis of $AlPO_4$-11

The $AlPO_4$-11 synthesis procedure[9] and structural characterisations[10] are described elsewhere. The following gel composition was used: 1 Al_2O_3 : 1 P_2O_5 : 1 dipropylamine : 70 H_2O. An aluminophosphate gel was prepared by adding the appropriate amounts of 85% orthophosphoric acid (Prolabo) and aluminium isopropoxide (99%, Aldrich) to distilled water. This mixture was stirred for 90 minutes before adding the templating agent, dipropylamine (DPA; 99%, Fluka). This final mixture was further stirred for 90 minutes before being transferred to a Telfon lined, stainless steel autoclave. This autoclave was placed into an oven and agitated at a temperature of 170 °C for 16 hours. Afterwards, the reaction mixture was filtered and washed thoroughly with distilled water before drying at 80 °C for 16 hours.

X-Ray diffractograms (STOE STADIP apparatus using a CuKα radiation source) of the as-synthesised sample (not shown) indicated a phase pure $AlPO_4$-11 product. SEM images were obtained with a Philips XL 30 apparatus and typically show agglomerates of around 4 µm in size (Fig. 1).

Sample controlled thermal analysis (SCTA)

In conventional thermal analysis, one measures a physical or chemical property "X" whilst a pre-determined program of heating is applied to the sample. In sample controlled thermal analysis (SCTA),[3] the roles of the "thermometer" and the "X-meter" are exchanged so that it is now the physical property "X" which is made to follow a predetermined program and thus controls the sample heating. The thermoanalytical information is obtained simply from the recording of the temperature with time. The property X that we consider here is the total pressure of evolved gases above the sample which originate from the rate of reaction itself. The rate of transformation can be selected at any value considered to be low enough to ensure negligible temperature and pressure differences within the sample bed.

The present study was carried out using Controlled Rate Evolved Gas Analysis (CR-EGA), which is a special case of SCTA.[11] The CR-EGA set-up used is described elsewhere[12] where the totality of gases evolved are analysed using a quadrupole mass analyser (VG quadrupoles) with a maximum detection of $m/z = 100$.

The experiments were carried out on *ca.* 20 mg samples under a residual pressure of 5×10^{-3} mbar. A typical experiment up to a final temperature of 750 °C took around 24 hours. Intermediate products were obtained by treating separate samples from the same initial batch up to 25, 100, 250, 370, 600 and 750 °C. For comparison, an experiment was carried out with the same apparatus at −30 °C with pure dipropylamine vapour.

FTIR spectroscopy

The infrared spectra were obtained using a Nicolet 205 apparatus in DRIFT mode on around 50 mg of sample under ambient conditions. The spectra obtained with the various samples were compared with a spectrum obtained with pure dipropylamine.

Adsorption manometry

Nitrogen adsorption–desorption isotherms at 77 K were determined with a commercial apparatus from ASAP 2010, Micromeritics S.A., France. The samples were outgassed prior to each experiment to a vacuum of 10^{-3} mbar. The temperature of outgassing was adapted to each sample according to the final calcination temperature.

Results

Sample controlled evolved gas analysis (SC-EGA)

Fig. 2 shows the results obtained from the SC-EGA experiment carried out with the as-synthesised $AlPO_4$-11. The temperature

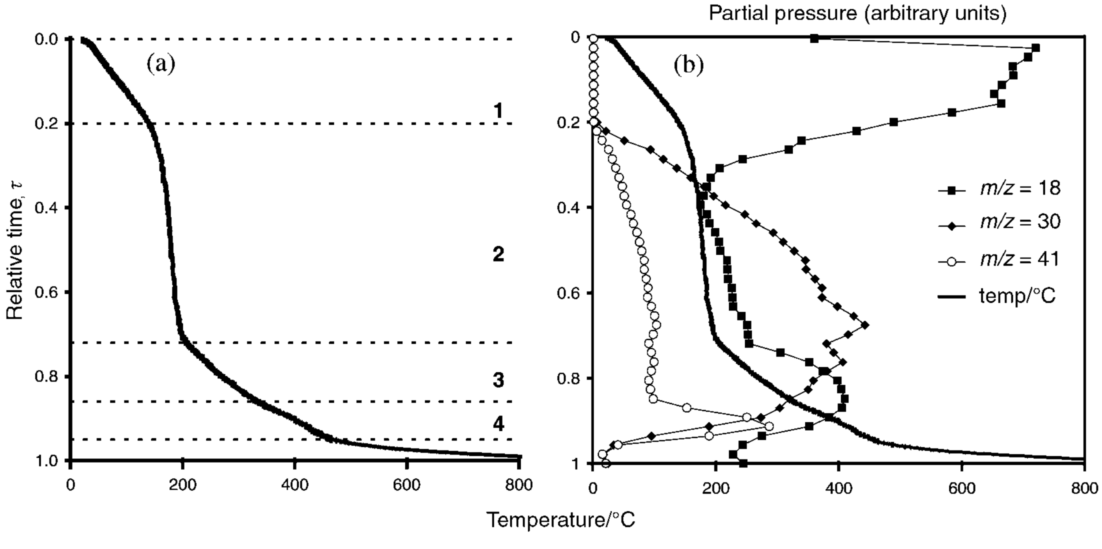

Fig. 2 SC-EGA temperature curve (a) and corresponding variation of several evolved species (b) as a function of τ for the thermal degradation of dipropylamine template occluded within $AlPO_4$-11.

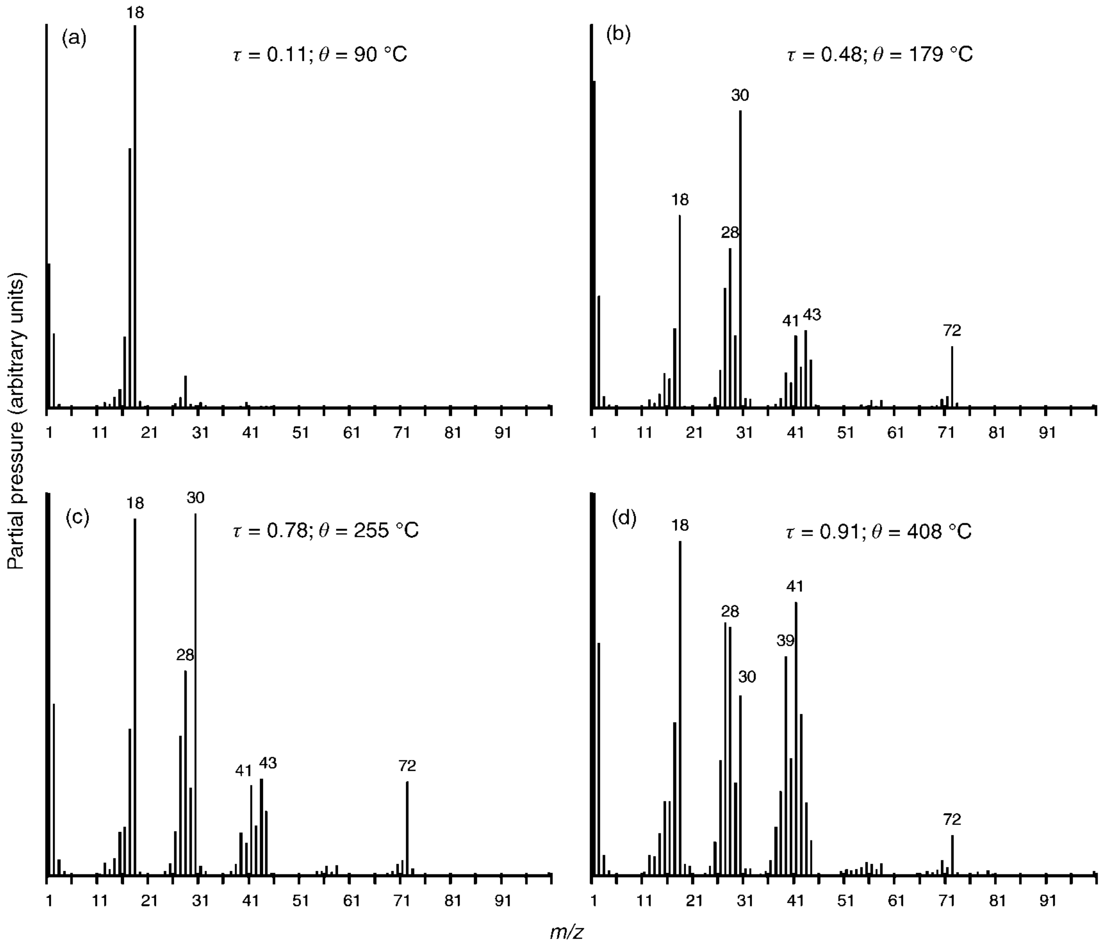

Fig. 3 Mass spectra obtained at various points during the thermal degradation of dipropylmaine template occluded within $AlPO_4$-11.

curve, obtained with the occluded dipropylamine, is presented as relative time τ ($= t/t_\infty$), as a function of temperature. Several significant m/z signals are also shown (Fig. 2b) which represent the various species that are eliminated during the reaction. The total mass spectra recorded at different points ($\theta = 90$, 179, 255 and 408 °C) are shown in Fig. 3. These spectra correspond to the four temperature domains visible in Fig. 2a and can be compared to the spectrum obtained with pure dipropylamine (Fig. 4) for which the main signals observed are $m/z = 28$, 30, 41, 43 and 72.

The SC-EGA curve can be split into four distinct regions denoted 1 to 4 (Fig. 2a). An initial region, 1, is observed from room temperature to around 140 °C and a degree of reaction of 0.2 (Fig. 2). This is accompanied principally by the loss of m/z signals 18, 17 and 16 (Fig. 3a) corresponding to water.

The main degradation occurs in region 2: $140 < \theta/°C < 210$ and to $0.2 < \tau < 0.72$. This region is marked by the increase in m/z signals corresponding to $m/z = 28, 30, 41, 43$ and 72 (Fig. 3b). It is noteworthy that, apart from the water signals, the spectra observed in this region of mass loss are similar to that observed for the pure dipropylamine vapour (Fig. 4). Indeed the intensities of the above-mentioned signals ($m/z = 28$, 30, 41, 43 and 72) relative to each other are the same in each case.

A third region, 3, from 210 °C to 330 °C ($0.72 < \tau < 0.86$) corresponds to the continued loss of dipropylamine species. Once again, the relative intensities of the species observed in this region and for the pure dipropylamine are the same. However, the m/z signals corresponding to water vapour increase once again (Fig. 3c).

The final region, 4, of degradation occurs from 330 °C to 470 °C under the chosen experimental conditions ($p = 5 \times 10^{-3}$ mbar). This corresponds to a changed mass spectrum pattern with notably the increase in signals corresponding to $m/z = 39$ and 41 and the decrease in $m/z = 43$ and 72 (Fig. 3d).

Fourier transform infra-red spectroscopy

Several samples were obtained at various temperatures, which were then analysed by FTIR (Fig. 5) under ambient conditions. As the heating protocol used leads to highly reproducible conditions, it is possible to consider the samples prepared as intermediates. The aim is thus to determine whether degradation species can be observed within the channels during the thermal treatment. As such it did not seem appropriate to carry out the spectra under vacuum to eliminate the large band due to water, around 3400 cm^{-1}. The as-synthesised sample (25 °C) shows peaks due to C–H: four peaks between 3260, 2980, 2938 and 2882 cm^{-1}. The N–H stretch bands at 3205 and 3107 cm^{-1} are relatively weak. As the thermal treatment temperature is increased, these peaks decrease until only a trace can be observed at 370 °C before complete loss at 600 °C. Furthermore, no distinguishable peaks due to degradation species occur in any of the spectra. However, a peak due to discrete –OH stretching is observed at 3606 cm^{-1} for the spectra taken with samples treated to 250 °C and higher. This band can not be attributed to either P–OH or Al–OH terminal groups, which appear at 3673 and 3793 cm^{-1} respectively in the case of two aluminophosphate samples: $AlPO_4$-5 [13] and $AlPO_4$-11.[14]

Adsorption manometry

The intermediate samples were analysed using nitrogen adsorption manometry at 77 K (Fig. 6). The experiments

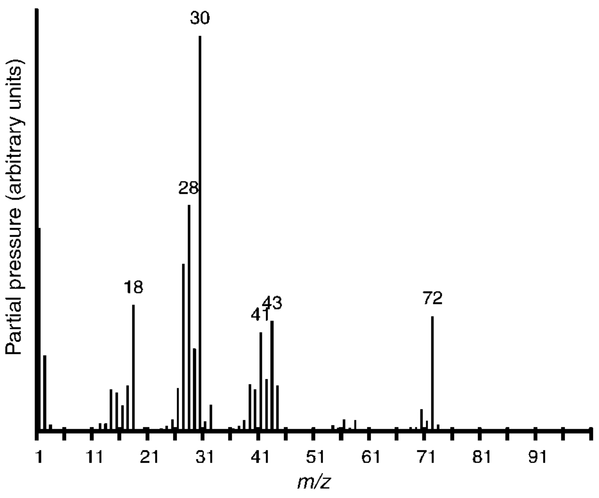

Fig. 4 Mass spectrum recorded with pure dipropylamine vapour at −30 °C.

were aimed to discern at what point and to what degree the porosity is liberated during the thermal treatment. Two distinct families of isotherms are obtained. For the samples treated up to and including 250 °C, the isotherms are of essentially type IV character[15] with a distinct hysteresis loop in the relative pressure region from 0.9 to 0.95. This hysteresis is observed with the as-synthesised sample before loss of any organic species and does not change on thermal treatment. It can thus be considered that this porosity corresponds to capillary condensation within the agglomerated particles observed by SEM (Fig. 1). It is only on treatment to 370 °C and higher that a change in the isotherms is observed. Indeed a distinct type I character is added to the type IV character previously noted, indicating the liberation of the micropososity.

Discussion

Region 1 from 25 °C to 140 °C

The initial region from 25 °C to 140 °C in the SCTA curve (Fig. 2) corresponds to the loss of water from the system. It is most probable that this water comes from the dehydration of the dipropylamine, hydrated during the hydrothermal synthesis.

Region 2 from 140 °C to 210 °C

This region in the SCTA curve corresponds to the loss of the majority of the organic template. It is interesting to note that both the mass spectra of the evolved species of the intermediates obtained in this region show features that are almost identical (with the exception of water) to the corresponding results obtained with the pure dipropylamine. This suggests the presence of hydrated dipropylamine species of the type $(C_3H_5)_2NH_2{}^+OH^-$.

It would seem from the above-mentioned results that the dipropylamine is liberated from the micropores of $AlPO_4$-11 without any degradation in this region. This may be due to a temperature induced evaporation type mechanism. The dipropylamine molecules are relatively linear and small enough to logically be able to diffuse through the pores. However, as noted earlier, this is not possible under vacuum alone. This temperature region (140–210 °C) is higher than the boiling point of the pure liquid (109–110 °C under atmospheric conditions) and this is certainly due to the confinement of these molecules, that is to say, due to the interactions between the molecules and the pore walls. Nevertheless, no degradation of these molecules is observed either on leaving the pores or whilst still confined inside.

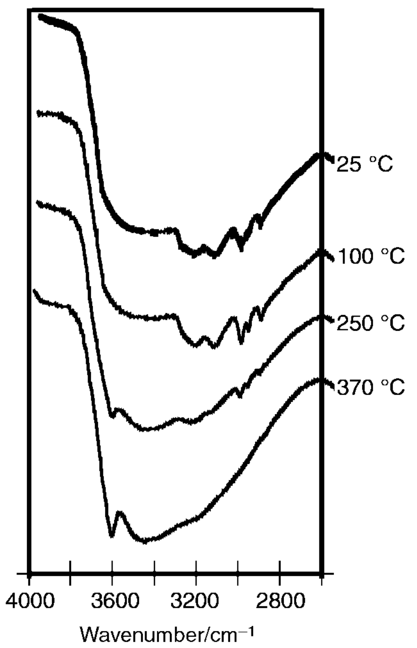

Fig. 5 FTIR spectra of the samples obtained at various intermediate temperatures during the thermal degradation of dipropylamine template from within $AlPO_4$-11.

The fact that an evaporation-type mechanism seems to be observed is rather an interesting point. Previous studies of the calcination of zeolites,[6,16] aluminophosphates[17] and the much larger mesoporous MCM-41 type materials[7,8,18] have all shown a degradation of the organic template *via* a Hofmann degradation type mechanism. These solids all have tertiary or quarternary amines as template molecules. Nevertheless, evaporation type mechanisms have been observed for the loss of alkylamines from α-zirconium phosphate intercalates.[19] It would seem that in the present case, as the aluminophosphate sample has a globally neutral framework and the secondary amine used here is a far more linear molecule, it is possible for the amine to leave the micropores without degradation.

Region 3 from 210 °C to 330 °C

This region of template loss corresponds to the increase in loss of water (Fig. 2) and to the formation of discrete –OH groups within the aluminophosphate as observed by FTIR (Fig. 5).

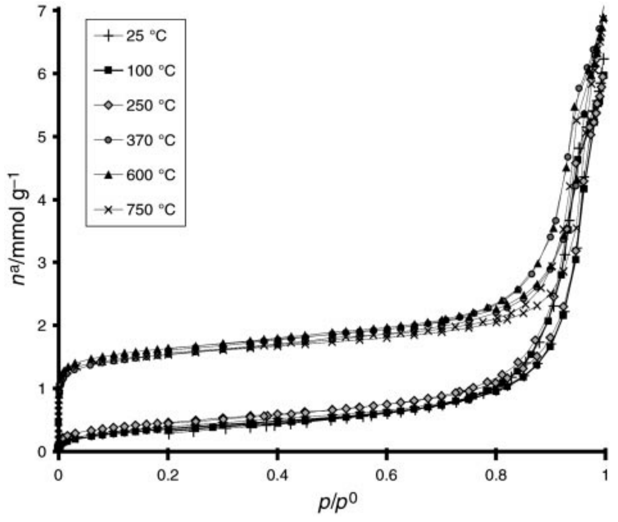

Fig. 6 Nitrogen isotherms for the samples obtained at various intermediate temperatures during the thermal degradation of dipropylamine template occluded within $AlPO_4$-11.

However, as for the previous step, no signs of degradation of the template species are observed either from the evolved gas analysis or from the infrared spectra of the intermediate samples. One can thus postulate that an evaporation type process again governs the dipropylamine loss. However, the change in shape of the temperature curve suggests a difference from the previous step (Region 2).

This may be explained if part of the hydrated dipropylamine is bound to the structure. This step would thus correspond to the liberation of this part of the template producing whole dipropylamine molecules and water. This latter explanation may explain the appearance of the –OH band in the infrared spectra for the sample isolated at 250 °C (Fig. 5). As stated above, it is possible to exclude the possibility of terminal P–OH and Al–OH sites responsible for the peak at $3606\,\mathrm{cm}^{-1}$. However, it is interesting to note that a band at $3605\,\mathrm{cm}^{-1}$ has been attributed to bridged hydroxyl groups (P–OH–Al) in the case of SAPO-34.[20] Such groups may be stabilised in the area of highest pore curvature. This would therefore suggest the possibility of $(C_3H_5)_2NH_2^+$ species linked to P–OH–Al groups.

The increase in the infra-red band around $3400\,\mathrm{cm}^{-1}$, resulting from sample rehydration, is due to the fact that the experiments were carried out under ambient conditions.

Region 4 from 330 °C to 470 °C

This region in the SCTA curve corresponds to the final loss of a small amount of template molecules. The infrared spectrum of the sample isolated at 370 °C indicates the absence of any organic species within the porosity even though some organic species are still observed during the on-line mass spectra analysis. It is also the point at which all of the microporosity becomes available to nitrogen adsorption. This would seem logical for a one-dimensional pore system where pore blocking is relatively simple with one molecule at each opening.

In this region, the mass spectrum of the evolved species changes with respect to that observed with pure dipropylamine with a relative increase in lower masses. This clearly indicates a certain amount of degradation of these species. If one takes into account the hypothesis that some of the template is bound to the aluminophosphate, then this region would correspond to the degradation of species that are relatively well bound to the surface. This may also explain the increase in intensity of the –OH stretch band observed in the infrared spectrum for the material isolated at 370 °C (Fig. 5).

Conclusions

This present study of the thermal treatment of dipropylamine occluded within $AlPO_4$-11 using sample controlled thermal analysis, under a residual pressure of 5×10^{-3} mbar, highlights a relatively interesting process of template loss. After an initial dehydration step, the large majority of the dipropylamine is liberated from the micropores in two steps (140–210 °C, 210–330 °C). It would seem that an evaporation type mechanism governs these losses as no evidence of any breakdown of the molecules is observed. This is certainly the result of the linear nature of the template molecule and could prove interesting for any process in which the recuperation of template is necessary. A small step from 330 °C to 470 °C is the first part where any indication of template degradation occurs. It is also in this region where all of the microporosity becomes free for nitrogen adsorption.

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