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THERMAL ANALYSIS OF SILICALITE-1 PRECURSORS

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ABSTRACT

Simultaneous thermal analysis (TG, DTG, DTA) in flowing air of the silica molecular sieve precursor TPA-silicalite-1 (TPA = tetrapropylammonium) shows that material crystallized at low temperature (95 °C) contains more silanol groups than the high-temperature (150 °C) product A single exotherm associated with the oxidative degradation of the TPA ion is obtained provided low heating rates or small sample sizes are used

INTRODUCTION

High-silica zeolites are prepared by the hydrothermal crystallization of alumino-silicate gels. The "as crystallized" zeolite precursor usually contains an organic template or void filler which must be removed to give the zeolite In most cases this is achieved by heating the zeolite precursor in air or under an inert atmosphere so as to decompose or volatilize the organic material Thermal analysis is ideal for the investigation of these processes, and it has been used by many workers to determine the mechanism by which the zeolite precursor is converted to the organic free zeolite [1,2] It is also used routinely in zeolite characterization [3–6] Such studies are almost invariably carried out with one sample size and a single heating rate, usually 10 °C min^{-1}, and the effects of either are rarely reported It is well known that both can have a pronounced effect on the results of thermal analysis experiments, and that they can often yield useful information about the processes involved [7] We have therefore investigated the role of these parameters in what we believe to be a typical but simple process the removal of the tetrapropylammonium (TPA) ion from the silicalite-1 framework by oxidative degradation

The silica molecular sieve silicalite-1 [8,9] has the same framework structure (*MFI*) as the high-silica zeolite ZSM-5 [10,11] In the sieve precursor the TPA ions occupy the channel intersections of which there are four per unit cell of 96 T-atoms (T = Al or Si), thus the stoichiometric composition of TPA-silicalite-1 is $(TPAOH)_4(SiO_2)_{96}$ To preserve electroneutrality the

TPA ion must be associated either with an hydroxide ion or (more likely) with a broken siloxane bond ($\equiv$ Si–O$^-$ HO–Si $\equiv$) When the TPA-silicalite-1 is heated to a sufficiently high temperature (in air or in an inert atmosphere) the organic material is completely removed and the lattice heals to give silicalite-1 [9,12] Most thermal analysis studies have been carried out with TPA-ZSM-5, and in this case the TPA ion may be associated with a framework aluminium site or a broken siloxane bond Consequently, separate decomposition processes might be expected for the ions in each environment and this has been observed both for the thermal decomposition under an inert atmosphere and the oxidative decomposition in air [13,14] In contrast, with TPA-silicalite-1 only a single exotherm is to be expected However, DTA measurements made with a Stanton Redcroft DTA674 with 50 mg samples in static air at a heating rate of 10 °C min^{-1} gave an exotherm which split irreproducibly into two or sometimes three peaks [15] This observation provided some of the stimulus for the work now reported

INSTRUMENTATION

Simultaneous differential thermal analysis (DTA), thermal gravimetric analysis (TGA), and differential thermal gravimetric analysis (DTG) were carried out with a Stanton Redcroft STA-780 series thermal analyser, used with a Servogor 460 four-channel chart recorder The equipment was interfaced via the chart recorder to a BBC model B + microcomputer which was used to collect DTA, TGA and DTG data as a function of both temperature and time Data points were collected at $\sim$ 1 °C intervals On completion of a run the data were corrected for baseline drift using base lines obtained for each heating rate with alumina in the sample and reference pans The corrected plots could be displayed on a VDU screen or output to a graph plotter (Linear Graphics Ltd , Plotmate A4M) The computer software, written in BASIC, allowed any combination of thermal analysis traces to be displayed over any chosen temperature range and permitted the accurate determination of the weight change between any pair of temperatures

All experiments were carried out in flowing air (30 cm^3 min^{-1}) using $\sim$ 16 7 mg of alumina in the reference pan The samples were evenly spread in the sample pan and ranged in weight from 4 to 31 mg The heating rate was fixed at values in the range 2 to 20 °C min^{-1} All experimental runs covered the temperature range 20–900 °C

MATERIALS

TPA-silicalite-1 was crystallized from the reaction mixture 10PIP 2TPABr 20SiO$_2$ 1000H$_2$O (PIP = piperazine) at 150 °C (material

P1) and 95 °C (material P2) Full details of the methods used to prepare these samples are given elsewhere [16,17] P1 consisted mainly of individual crystals with dimensions ~ 20 × 6 × 4 μm, while P2 contained mainly twinned crystals with individual crystal dimensions of ~ 10 × 7 × 4 μm X-ray powder diffraction patterns showed P1 and P2 to be highly crystalline TPA-silicalite-1, and they appeared from scanning electron microscopy completely free from amorphous material Before thermal analysis both materials were equilibrated in vacuo with water vapour (saturated NaCl solution, 25 °C, $a_w = 0\ 753$)

RESULTS AND DISCUSSION

TGA curves were obtained for P1 and P2 over a series of heating rates and sample sizes Typical examples are shown in Fig 1 The curves were found to be essentially independent of the heating rate Table 1 gives the weight losses over selected temperature ranges, and shows that these are reproducible to within ± 0 3% and independent of the sample size However, with smaller samples problems were encountered with signal noise and the base line correction became difficult to apply The upper limit is determined by the crucible size, and although no adverse effects were observed with tightly packed samples, there was no advantage to be gained by using a sample larger than 15 mg With this equipment we find the optimum sample size for the TGA of zeolites is ca 10–15 mg

Without additional information, the exact interpretation of the TGA curves is difficult The low temperature weight loss is considered to be due

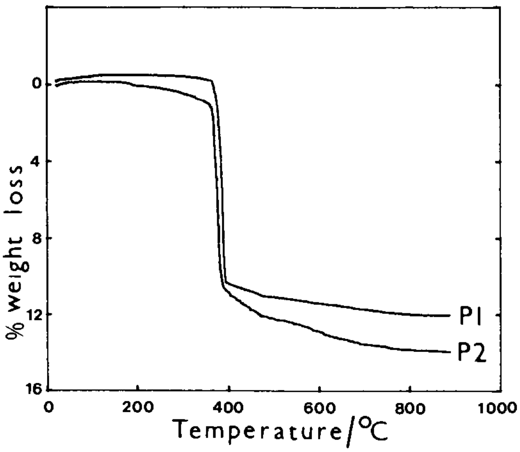

Fig 1 TGA curves for TPA-silicalite-1 P1 (18 17 mg) and P2 (16 31 mg) (heating rate 10 °C min^{-1})

TABLE 1

Thermal analysis results for TPA-silicalite-1

Material	Sample weight (mg)	Peak temperature (° C)			Weight loss (%) over temperature ranges (° C)			
		DTG	DTA	DTA	0–350	350–410	410–600	600–900
P1	4 27	402	–	401	0 2	10 5	0 8	0 6
P1	7 61	398	394	397	0 2	10 8	0 9	0 4
P1	10 62	395	391	395	0 2	11 0	0 9	0 6
P1	13 98	390	385	391	0 3	10 7	0 9	0 7
P1	18 17	390	384	395	0 4	10 5	1 1	0 7
P1	31 12	393	383	398	0 4	10 5	1 1	0 8
P1	Average				0 3±0 1	10 7±0 3	0 9±0 2	0 6±0 2
P2	5 80	381	–	380	0 8	10 2	1 6	1 1
P2	10 67	378	–	379	1 0	10 3	1 8	1 0
P2	14 03	376	369	378	1 0	10 5	1 8	1 1
P2	16 31	380	367	382	0 9	10 5	1 6	1 0
P2	19 89	374	366	379	1 2	10 1	2 1	1 2
P2	22 64	379	367	384	0 9	10 2	1 8	1 3
P2	Average				1 0±0 2	10 3±0 2	1 8±0 3	1 1±0 2

to occluded water, and that above 350 ° C to organic material and chemically bound (or structural) water If the TPA-silicalite had the ideal stoichiometric composition $(TPAOH)_4(SiO_2)_{96}(H_2O)_x$ where x is the number of occluded water molecules per unit cell the percentage weight loss above 350 ° C would be 12 24 for P1 and 12 32 for P2, whereas the actual values are 12 3 ± 0 3 and 13 2 ± 0 3, respectively Hence, at least in the case of P2, the weight loss above 350 ° C cannot be accounted for in terms of the proposed ideal composition As it is impossible for the unit cell to contain more than four TPA ions, part of the weight loss must be due to other species In an earlier investigation [15] a material prepared in the same way as P2 exhibited a similar discrepancy which was interpreted in terms of occluded piperazine For sample P2 the percentage weight loss could be accounted for by the composition $(TPAOH)_{3\ 45}PIP_{2\ 20}(SiO_2)_{96}(H_2O)_{3\ 73}$ This assumes four piperazine molecules are occluded instead of one TPA ion However, in the present case the DTA curves do not show the broad peak at 500–650 ° C ascribed to piperazine Furthermore, the ^{13}C MASNMR spectra of other samples of TPA-silicalite-1 prepared from similar reaction mixtures do not show the presence of piperazine Hence, it is necessary to seek other interpretations of the TGA curves

The weight loss above 350 ° C occurs in four stages, a very sharp loss to ~ 390 ° C, a more gradual one to 410 ° C, and shallow ones above and below 600 ° C DTA (see later) shows that the decrease in weight from 350 to 410 ° C is accompanied by an exotherm and hence corresponds to the oxidative degradation of the organic species Thus, it is unlikely that any organic material remains in the lattice above 600 °C and the weight loss from 600 to 900 °C must be due to external and internal silanol groups Although the weight loss between 410 and 600 °C is not associated with an exotherm in the DTA it seems likely that at least part of it could be caused by the loss of organic material Although the mechanism for this process is not understood it is suggested that it takes place in two stages

$$\mathrm{TPA^+(\equiv Si{-}O^-\ HO{-}Si\equiv) \rightarrow (\equiv Si{-}OH\ HO{-}Si\equiv) + volatile\ products} \qquad (1)$$

$$\mathrm{(\equiv Si{-}OH\ HO{-}Si\equiv) \rightarrow (\equiv Si{-}O{-}Si\equiv) + H_2O} \qquad (2)$$

A recent paper [18] reports that the silanol groups produced by reaction (1) are present after calcination at 538 °C, and although it is possible that in favourable circumstances (e g high water levels consequent on combustion of the TPA ion [18]) reaction (2) occurs below 600 °C, most of the silanol groups must be lost at higher temperatures Hence it is possible to calculate a lower limit to the amount of TPA present on the assumption that all of the 350 – 410 °C weight loss is due to reaction (1) The unit cell compositions

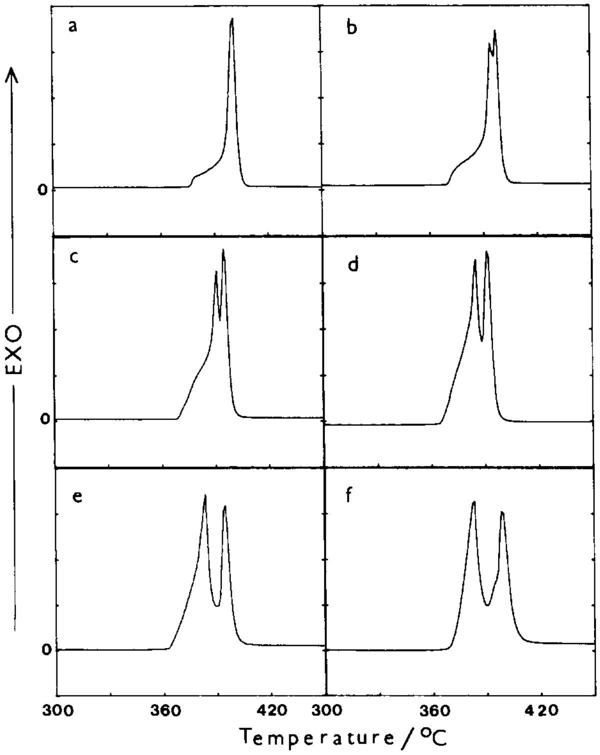

Fig 2 DTA curves for TPA-silicalite-1, P1 (heating rate 10 °C min^{-1}) for sample sizes (a) 4 27 mg, (b) 7 61 mg, (c) 10 62 mg, (d) 13 98 mg, (e) 18 17 mg, (f) 31 12 mg

obtained in this way are for P1 $(TPAOH)_{3\,81}(SiO_2)_{96}(H_2O,oc)_{1\,10}(H_2O,str)_{1\,68}$ and for P2 $(TPAOH)_{3\,74}(SiO_2)_{96}(H_2O,oc)_{3\,73}(H_2O,str)_{7\,09}$ where oc and str denote occluded and structural water, respectively However, it is possible that not all of the organic material is removed below 410 ° C, and that the actual TPA content is much closer to four molecules per unit cell In the case of P1 the composition $(TPAOH)_{3\,95}(SiO_2)_{96}(H_2O,oc)_{1\,10}(H_2O,str)_{0\,00}$ would be obtained if all the weight loss above 350 ° C were ascribed to TPAOH For P2 the weight loss above 350 ° C is so large that it cannot all be due to TPAOH, if we assume there are four TPA ions per unit cell we obtain $(TPAOH)_4(SiO_2)_{96}(H_2O,oc)_{3\,73}(H_2O,str)_{4\,10}$ It seems likely that at some temperatures reactions (1) and (2) may occur simultaneously, and that it is not possible to choose a specific temperature at which one reaction ceases and the other starts, consequently one can only establish a range of compositions for P1 and P2 Nevertheless, the results show clear differences between the two materials, P2 which was crystallized at the lower temperature contains much more occluded and structural water than P1 and, although not apparent from the X-ray powder diffraction pattern and the

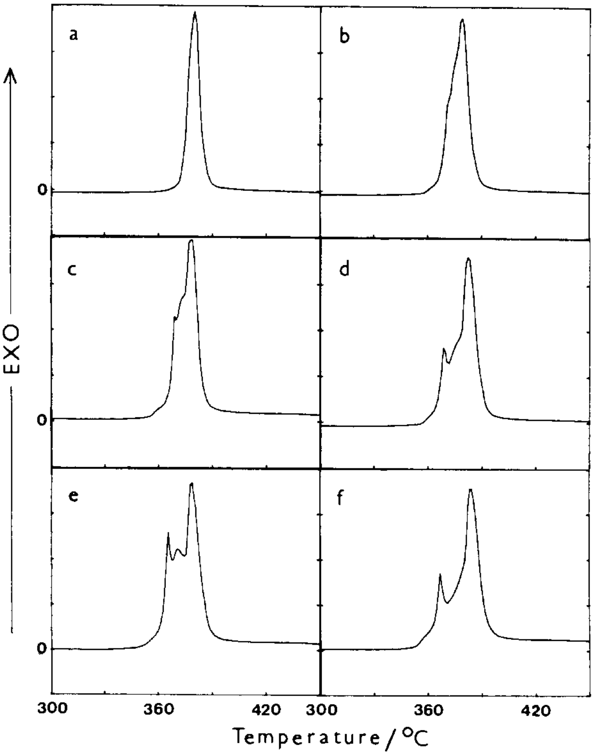

Fig 3 DTA curves for TPA-silicalite-1, P2 (heating rate 10 ° C min^{-1}) for sample sizes (a) 5 80 mg, (b) 10 67 mg, (c) 14 03 mg, (d) 16 31 mg, (e) 19 49 mg, (f) 22 64 mg

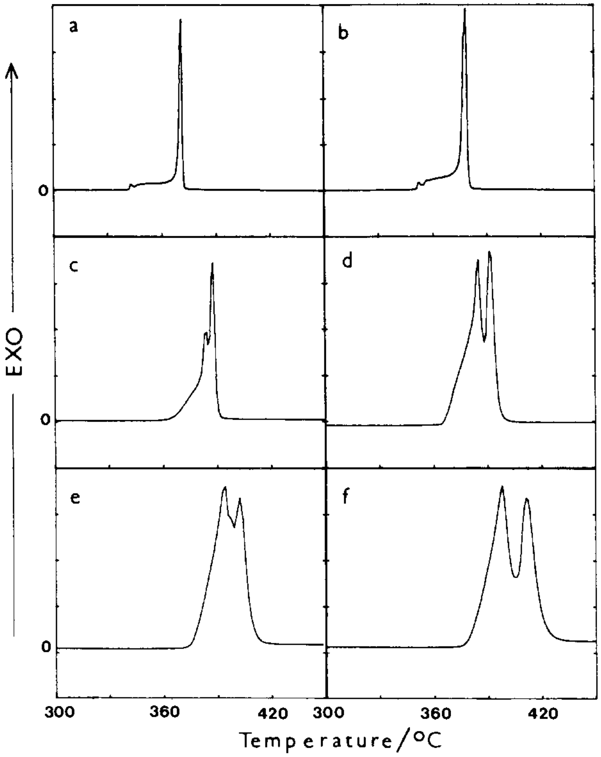

Fig 4 DTA curves for TPA-silicalite-1, P1, at different heating rates (a) 14 17 mg, 2 °C min^{-1}, (b) 14 01 mg, 3 °C min^{-1}, (c) 13 94 mg, 5 °C min^{-1}, (d) 13 98 mg, 10 °C min^{-1}, (e) 14 10 mg, 15 °C min^{-1}, (f) 13 92 mg, 20 °C min^{-1}

scanning electron micrographs, it may contain some amorphous silica On the other hand, P1 appears to be a more perfect material, free from broken siloxane bonds other than those associated with the TPA ions

Initial DTA measurements in flowing air with 10–15 mg samples at a heating rate of 10 °C min^{-1} gave exotherms which were split in a similar fashion to those observed in previous work [15] To establish whether this splitting was an intrinsic property of the material or a consequence of the operating conditions the two preparations of TPA-silicalite-1 (P1, P2) were examined with different heating rates and with a range of sample sizes

Figures 2 and 3 show that at a constant heating rate the splitting of the exotherm is indeed a function of sample size For both P1 and P2 the splitting decreases as the sample size is reduced and is non-existent for the smallest sample ($\sim$ 5 mg) The splitting is more pronounced in the case of sample P1 which has the larger crystals and the lower water content Figure 4 shows that with a constant sample size the splitting diminishes as the heating rate is reduced and at the lowest heating rate a sharp peak is observed With both materials and with all sample weights and heating rates there was only one DTG peak (Table 1) For the smallest sample weights and the lowest heating rates the DTA and DTG peaks coincide (Table 1), for larger sample sizes and higher heating rates the DTG peak falls between the two DTA peaks Thus, the observed effect is apparent in the DTA but not in the DTG This is consistent with temporary shortage of oxygen when the rate of organic decomposition approaches its maximum It appears that the removal of TPA from the silica framework takes place in two steps, an initial cracking process, possibly

$$\equiv \mathrm{Si{-}O^{-}TPA^{+}} \rightarrow \equiv \mathrm{Si{-}OH} + (\mathrm{C_3H_7})_3\mathrm{N} + \mathrm{C_3H_6} \qquad (3)$$

followed by oxidation of the fragments as they leave the crystals Thus, the materials can continue to lose weight despite the lack of air to oxidize the products

At the lowest heating rates, or with the smallest sample sizes, material P1 (Figs 2 and 4) shows a small flat exotherm in advance of the main peak This appears to be related to an intrinsic, but so far unidentified, property of the material, which is absent in the case of P2

CONCLUSIONS

The results show that samples of TPA-silicalite-1 crystallized at different temperatures can show marked differences in their thermal behaviour At least three components, occluded and structural water and the organic template, contribute to the weight loss All three may overlap, and it is particularly difficult to apportion the weight loss between the organic material and the structural water This problem cannot be solved by changing the heating rate or the sample size, as both have minimal effects on the TGA curve For TG the optimum sample size for high-silica zeolite precursors on the STA780 thermal analyser is 10–15 mg, and a heating rate of 10 °C min^{-1} is satisfactory However, in the DTA the major exotherm is split, probably through oxygen starvation, unless the heating rate is low (2 °C min^{-1}) or the sample size small (5 mg) For simultaneous thermal analysis the best compromise is a sample size of 10 mg and a heating rate of 2 °C min^{-1}

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