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THE EFFECT OF GRINDING ON THE THERMAL BEHAVIOUR OF TETRAPROPYLAMMONIUM OCCLUDED IN SILICALITE 1.

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ABSTRACT

In this paper, it is investigated the effect of grinding on the thermal decomposition of tetrapropylammonium ions occluded in silicalite 1, in order to shed more light on the nature of the TPA species associated with peaks B, C1 and C2.

INTRODUCTION

The organic compounds used as either structure-directing and/or space filling species in high silica zeolites synthesis, are generally occluded in the zeolitic channels and cavities either in an intact or in a modified state [1,2]. The state of tetrapropyl (TPA) ions occluded in ZSM-5 channels has been most thoroughly investigated by thermal analysis combined with mass spectrometry [3] or ^{13}C N.M.R. spectroscopy [4]. It was concluded, that the DTA peak C1 (Fig. 1) at a temperature smaller than ca. 440 ^{o}C is due to defect SiOTPA groups, while peak C2 ($T>440$ ^{o}C) is characteristic of those TPA ions which neutralize the framework $(Si-O-Al)^{-}$ negative charges [3,4]. In addition, it was also suggested, that the high temperature C2 peak also includes some more relaxed TPA ions which are obtained after the decomposition of ca. half of their initial amount (4 TPA/u.c.) [4]. These species are of course the main contributors to peak C2 in a high silica ZSM-5 (or silicalite 1) [4]. They were characterized previously by ^{13}C N.M.R. spectroscopy only [5].

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Nevertheless, during partial decomposition of TPA ions, some products of decomposition (tripropylamine, propylene....) are still occluded in the zeolitic channels in both ZSM-5 and silicalite 1 [4]. On the other hand , the temperature of peak C1 seems to be influenced by the Si/Al ratio, and hence the number of defect grooups formed during synthesis [6]. Finally peak B was attributed to TPA species occupying the external shell of the crystallites [7].

In this paper , we report the effect of grinding on the thermal behaviour of TPA ions occluded in silicalite 1, in order to shed more light on the nature of the TPA species associated with peaks B, C1 and C2.

EXPERIMENTAL

Large crystals of various size were synthesized from a batch 11TPABr- $10Na_2O$-$100SiO_2$-$2490H_2O$ [8]. To a 50 wt % NaOH solution (Fischer Chemical) is added TPABr (Aldrich) and ca 20 g of distilled water. To this solution colloidal SiO_2 (Ludox AS-40, du Pont) is added under continuous stirring. The final mixture was a uniform clear solution in most of the cases. The final solutions were poured into 15 ml Teflon-lined Morey-type reaction vessels, sealed immediately and placed into a forced convection oven preset to 185 °C. Upon completion of the reaction (one week for all runs), vessels were removed and immediately quenched under cold tap water. The product crystals were washed five times with 50 ml of distilled water and dried overnight.

The nature and crystallinity of the solid phases were determined using X-ray powder diffraction patterns,recorded on a Philips PW 1349/30 diffractometer controlled by Olivetti M24 computer, using Cu-Kα radiation, and 0.50 2 tetha per minute.10% $Pb(NO_3)_2$ was used as internal standard.

Thermal analyses DTA TGA DTGA, were recorded on a Netzsch STA 429 thermal analyser controlled by H.P. 86 computer (nitrogen flow: 15 ml/min; heating rate 10 °C/min).

RESULTS AND DISCUSSION

The Table 1 shows, that in most of the cases the initial amount of TPA/u.c. (ca. 4) generally decreases (from 5 to 12 %)

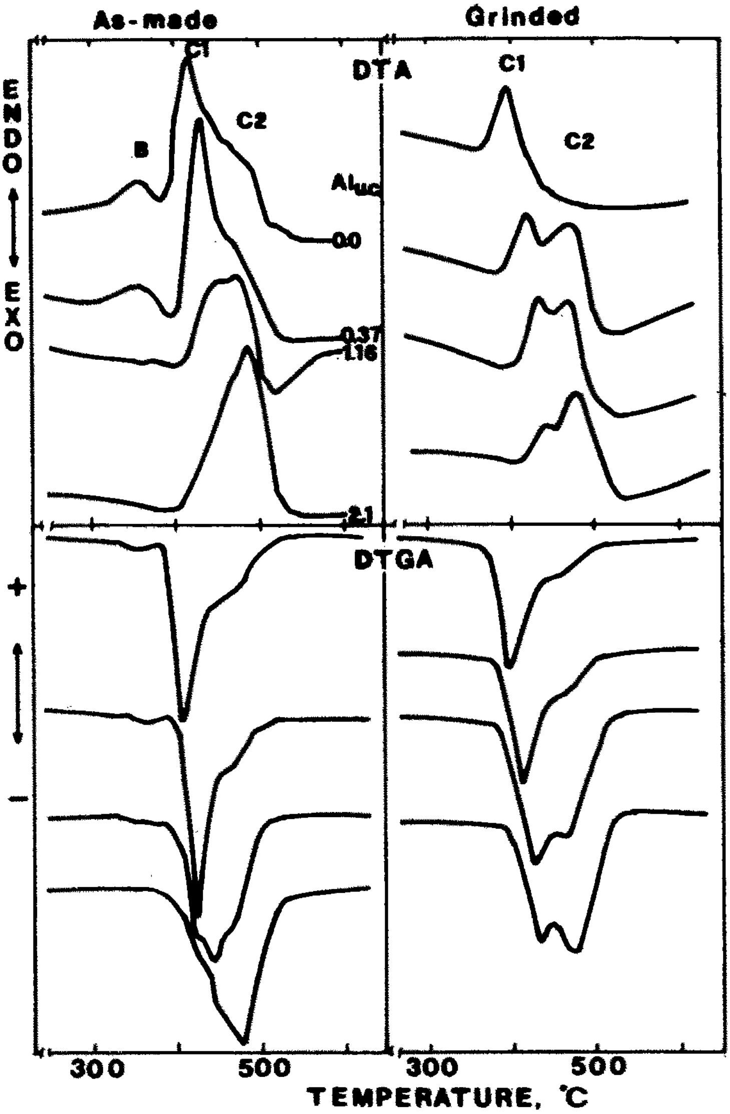

Fig. 1. DTA and DTG curves of TPA ions occluded in silicalite crystals: 1) as-made crystals of 100 μm diameter 2) grinded crystals of ca < 5 μm diameter.

TABLE 1

Thermal analysis data of as-made and grinded silicalite samples

Crystal size (μm)	$TPA_{u.c.}$	TPA_{uc} peak B	peak C1	peak C2	Temperature ranges peak C1(°C)
1) 15	3.9	0.2	2.9	0.8	415 - 460
2)	3.7	-	3.0	0.7	375 - 460
1) 35	4.0	0.2	2.5	1.3	400 - 480
2)	3.7	-	2.6	1.1	370 - 470
1) 100	4.0	0.2	2.1	1.7	390 - 430
2)	3.8	-	2.9	0.9	390 - 455
1) 140	4.2	0.2	2.3	1.7	385 - 430
2)	3.7	-	2.4	1.3	390 - 440
1) 180	4.0	0.2	2.7	1.1	390 - 460
2)	3.7	-	2.8	0.9	365 - 465
1) 250	4.1	0.1	2.5	1.5	380 - 440
2)	3.7	-	2.7	1.0	385 - 485

Initial temperature for peak C2 is the final temperature for peak C1 and the final temperature for peak C2 is always 540 °C.

upon grinding. In addition, changes can also be noted in the relative amounts of peaks B, C1 and C2 (Fig. 1). (Actually, the relative amount of peak B is difficult to determine for the grinded samples, hence there values are not reported in the Table 1). Peak B decreases upon grinding, peak C1 shows a slight increase, and peak C2 is generally the most influenced one, it decreases upon grinding (Fig. 1 and Table 1).

Peak B was attributed previously to TPA species occupying the external shell of the crystallites [7]. Consequently, this peak should increase then upon grinding, because the total surface of the crystallites increases. In fact the dimension of the crystallites after grinding is decreased to <5 μm in all of the cases. Because of the significant decrease in peak B, another explanation has to be sought for. It is now well known, that ZSM-5 crystals, and even more the silicalite crystals, do incorporate a rather large amount of SiOR defect groups (R=H, alkali cations, TPA) in their structures [7, 9]. The amount of the defect groups can be as large as 32/u.c. in silicalite [7] corresponding to ca. eight missing tetrahedral sites [9]. This means that macrocavities could be formed in these zeolites, where the TPA cations are less strongly held than in the zeolitic channels and hence, their thermal decomposition is easier. These macrocavities are mostly eliminated upon grinding and the intensity of peak B decreases.

Peak C1 is attributed to TPA^+ ions neutralizing the inner SiO^- defect groups [3,4]. The slight increase upon grinding can be explained by the easier decomposition of these species as well as the easier elimination of the decomposition products.In the case of initially large crystals, the decomposition products are not easily eliminated and the intensity of peak C2 is rather high. After grinding,this peak decreases,and the remaining contribution can now essentially be attributed to the decomposition of more relaxed TPA species occurring at higher temperatures [4]. Hence, peak C2 for large crystals is attributed to both the elimination of the decomposition products of the SiOTPA groups and the decomposition of the more relaxed TPA species.

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