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THERMAL BEHAVIOUR OF THE TPA IONS IN ZSM-5 ZEOLITE: I. EFFECT OF THE Si/Al RATIO AND GRINDING

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Thermal decomposition of tetrapropylammonium (TPA) ions, as a function of the Si/Al ratio and the grinding of ZSM-5 crystals, was investigated by DTA and DTG analyses. The amount and the temperature decomposition of TPA ions, such as the crystal size, increase with increasing Al/u.c. The grinding of ZSM-5 crystals lowers the temperature decomposition of TPA ions. Considerations on experimental results are reported.

Zeolite ZSM-5 is generally synthesized by hydrothermal crystallization of aluminosilicate gels. Even though it has also been prepared in the absence of organic base cations [1], tetrapropylammonium (TPA) is usually employed in the synthesis process.

The clathrating and templating effects of organic cations (e.g. tetrapropylammonium) in the synthesis of ZSM-5 zeolites are rather well described in the current literature [2, 3]. In particular, the interaction of TPA ions with amorphous gel phases [3] and with the crystalline ZSM-5 framework [4-6] has been treated in more details. In fact, the residual gel, normally present in the synthesized products, can influence the activation of zeolitic catalysts and the catalytic properties of ZSM-5 crystals [7].

In this paper, it is investigated how the thermal decomposition of TPA ions is influenced by the Si/Al ratio and the grinding of ZSM-5 crystals.

Experimental

The ZSM-5 samples were synthesized at 170° under autogeneous pressure for given periods of time using Teflon autoclaves from a system: $4Na_2O$-8TPABr- xAl_2O_3-$100SiO_2$-$1000H_2O$ with x ranging from 0 to 4. The final products were characterized by X-ray diffraction and chemical analysis. The

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residual amorphous phase was separated from the crystals by ultrasound treatment. The effectiveness of the treatment was checked through scanning electron microscopy and optical microscopy analyses. The thermal analyses were carried out under nitrogen atmosphere by an automatic thermal analyzer (NETZSCH STA 449) linked to a HP 86B computer. The following experimental conditions were used: sample weight: 100 mg; sample holder: platinum crucible; reference material: calcined kaolin; temperature range 25-700°; heating rate 10 deg/min; nitrogen flow rate 15 cm^3/min.

Results and discussion

Figure 1 shows the DTA and DTG patterns of the sonicated pure crystals and of the corresponding ground ZSM-5 samples with x = 0; 0.5; 2.0 and 4.0. Quite important changes can be noted on both the DTA and DTG curves as a function of Al/u.c. Peak B (at ca. 360°) increases systematically with decreasing Al content. On the other hand, it is known that the amount of SiOR defect groups (R = H, alkali cations, TPA) also increases with decreasing Al/u.c. [8]. The TPA species which decompose at this temperature are then believed to occupy the macrocavities where a large amount of defect groups can be found, as suggested by N.M.R. results reported elsewhere [9]. The fact that their thermal decomposition is easier indicates that these cations are less strongly held.

The effect of Al/u.c. can also be noted on the temperature of peak C1 and on the relative intensities of peaks C1 and C2 (see Figs 1 and 2). Peak C1 (at lower temperature) is attributed to TPA ions neutralizing SiO- defect groups, while C2 (at higher temperature) is due to TPA + ions neutralizing framework $(Al\text{-}O\text{-}Si)^-$ negative charges. These findings are in line with those obtained by combined DTA and N.M.R. analysis on other systems [5]. The temperature of peak C1 increases with increasing Al/u.c. This is likely due to the decreasing of the number of defect groups. In fact, it has been found that the number of defect groups decreases from ca. 32/u.c. for very low Al content samples, to ca. 10/u.c. for a sample with Al/u.c. = 2 [8]. It is then obvious, that the decomposition of TPA ions becomes more difficult for high Al content samples and hence, the temperature of decomposition increases.

The increase in Al/u.c. is also accompanied by an increase in the relative amount of TPA^+ ions which neutralize the framework $(Al\text{-}O\text{-}Si)^-$ negative charges (see Fig. 1). Note, that peak C2, in addition to these species, also contains more relaxed TPA^+ ions, which are left after decomposition of ca.

half of the initial TPA amount, as well as some products of the TPA decomposition (tripropylamine, propylene,...) [5, 6].

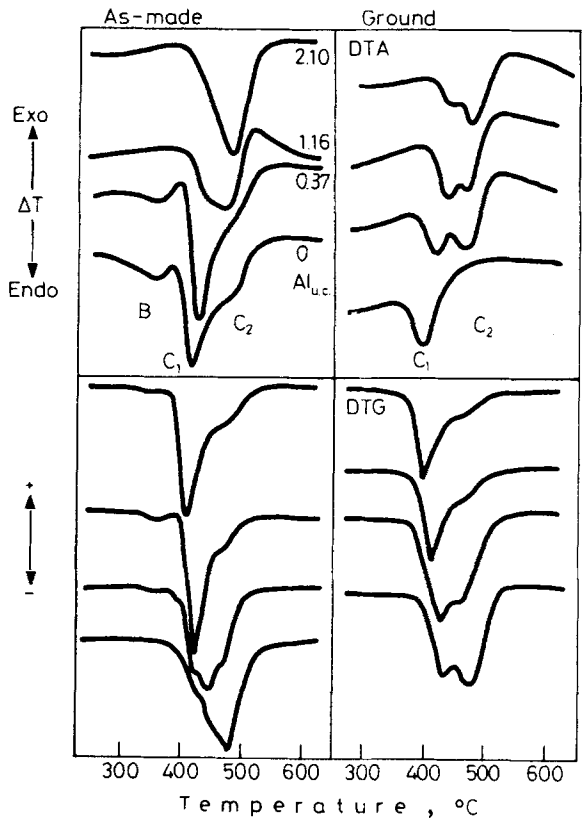

Fig. 1 DTA and DTG curves of the sonicated pure crystals and of the corresponding ground ZSM-5 crystals as a function of Al/u.c.

The relative amount of the decomposition products should of course increase with increasing crystallite size. This is indeed the case, as the crystal size also increases with increasing Al/u.c. (see Fig.2).

The effect of grinding can be noted by the quasi disappearance of peak B, the change in the relative amounts of TPA associated with peaks C1 and C2 (see Fig. 1) and the decrease in temperature of peak C1 (see Figs 1 and 2).

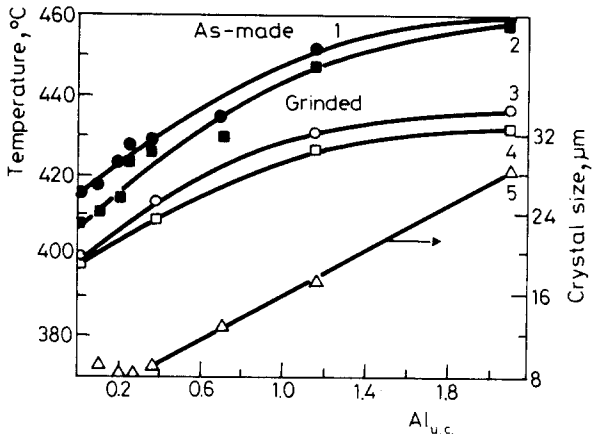

Fig. 2 Variation of the temperature of DTA (1, 3) and DTG (2, 4) peaks of C1 and of the crystal size (5) as a function of Al/u.c.

The quasi disappearance of peak B upon grinding was also noted on large silicalite crystals [9]. It has been interpreted by the elimination of the large macrocavities. The grinding lowers the temperature of peak C1 more effectively than that of C2 leading to a better resolution of the DTA and DTG peaks. The temperature lowering of peak C1 can be explained by the decrease of crystal dimension after grinding ($d < 5\ \mu m$), resulting in an easier evacuation of the decomposition products of TPA^+ ions.

In addition, the TPA/u.c., computed from peaks C1 and C2, decreases drastically and the relative intensity of peak C1 is greatly decreased in comparison to that of peak C2. This can be explained by the fact, that during grinding the ZSM-5 crystals are preferentially cleaved along SiOR defect lines, eliminating consequently part of the TPA^+ ions linked to these defect groups. The so-eliminated TPA^+ ions are then deposited on the surface and are continuously decomposed between 200 and 400° and their amount corresponds to ca. 0.5/u.c. The TPA^+ ions neutralizing the framework $(Si\text{-}O\text{-}Al)^-$ negative charges are rather unaffected by grinding. Note also, that the crystallinity also decreases upon grinding as it can be inferred from the decrease of the total TPA/u.c.

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Zusammenfassung — Mittels DTA und DTG wurde die thermische Zersetzung von Tetrapropylammonium- (TPA) Ionen als eine Funktion des Si/Al-Verhältnisses und der Zerkleinerung der ZSM-5 Kristalle untersucht. Grad und Temperatur der Zersetzung der TPA-Ionen wachsen mit steigendem Al-Gehalt an. Eine Zerkleinerung der ZSM-5 Kristalle senkt die Zersetzungstemperatur der TPA-Ionen.