

THERMAL BEHAVIOUR OF THE TPA IONS IN ZSM-5 ZEOLITE: II. EFFECT OF CRYSTAL SIZE AND GRINDING OF SILICALITE-1

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Thermal decomposition of Silicalite-1 crystals of various size was studied. The crystals were in as-made form and upon grinding. The DTA and DTG curves show differences in the temperature of thermal decomposition of TPA species occluded in the as-made crystals. These differences disappear upon grinding. The explanation of this phenomena is given.

Silicalite-1, the Al-free analogue of ZSM-5 zeolite was first prepared by E. M. Flanigen *et al.* [1]. It has the same crystal structure as the ZSM-5 zeolite which has been applied as a catalyst in MTG and other petrochemical processes [2].

Synthesis of the ZSM-5 zeolite and its aluminium deficient end-member silicalite has been the topic of a large number of investigations [3]. The parameters affecting the growth of large silicalite crystals and the effect of reactant concentration on crystal morphology have been reported by Hayhurst *et al.* [4, 5].

The organic compounds used as either structure-directing and/or space filling species in a high-silica zeolite synthesis are generally occluded in the zeolite channels and cavities either in an intact or in a modified state [3, 6]. The state of tetrapropylammonium (TPA) ions, occluded in ZSM-5 channels has been most thoroughly investigated by thermal analysis combined with mass spectrometry [7] or ¹³C-NMR spectroscopy [8]. TPA ions decompose by the Hoffman reaction to give an olefin and trialkylamine [7].

The three DTA peaks (B, C1 and C2) have been assigned [8] to decomposition of different TPA species occluded into the zeolitic channels. In the case of Al-free silicalite, the low temperature (ca 380°) peak B is attributed [9] to less strongly held or "outer shell" strained TPA ions. A peak C1 (ca. 425°) is assigned to inner ions neutralizing SiO⁻ negative charges of

defect groups. The high temperature peak C2 (ca. 475°) is attributed to decomposition of TPA in "relaxed" form, although it also neutralizes SiO⁻ defect groups.

In the present paper we have studied the influence of the silicalite crystal size on the TPA decomposition temperature.

Experimental

Silicalite crystals of 15, 100, 140 and 250 μm were synthesized from a batch composition 11 TPABr - 10 Na₂O - 100 SiO₂ - 2490 H₂O [4]. The reagent used were: colloidal SiO₂ (Ludox AS40, Du Pont), NaOH (Fischer Chemical), TPABr (Aldrich). The gels were heated in 15 ml Teflon-lined Morey-type reaction vessels for one week at 185°. Upon completion of the reaction, vessels were removed from convection oven and quenched under cold tap water.

The ZSM-5 structure of the crystalline material obtained has been confirmed by XRD (Philips PW 1349/30 diffractometer using Cu-K α radiation and 0.50 2 Θ per min.). Thermal analyses DTA, TG, DTG were recorded on a Netzsch STA 449 thermal analyser controlled by HP 86 computer (nitrogen flow 15 ml/min, heating rate 10 deg/min). The crystal size was evaluated by an optical microscope.

Results and discussion

The results of thermal analyses are given on Figs 1 and 2.

The TPA content per unit cell (96 SiO₂), as determined from the weight loss upon calcination is quite close to the theoretical number of 4. This value decreases upon grinding.

The DTA and DTG results of sample 4 (250 μm) are illustrated on Fig. 1. The DTA curve shows two distinct endotherm: B at 380° and C1 at 418°. A peak C2 is in the form of a shoulder at the temperature of about 460°. On the DTG curve, there is only one distinct peak at 414° and two shoulders at lower and higher temperatures.

Figure 2 illustrates the DTA curves of large silicalite crystals in as made form and upon grinding. The larger are the crystals, the lower is the temperature of their C1 endotherm. Sample 1 (15 μm) has a peak C1 temperature at 434°, sample 2 (100 μm) at 423°, sample 3 (140 μm) at 420° and sample 4 (250 μm) 418°. Upon grinding, when the crystal size of all

samples has been decreased to $<5\ \mu\text{m}$, the C1 endotherm is $426\text{--}428^\circ$ for all four samples investigated.

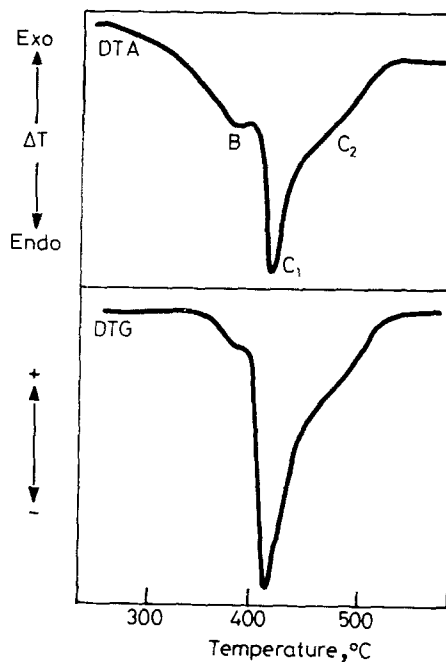


Fig. 1 DTA and DTG curves of $250\ \mu\text{m}$ crystal size Silicalite 1 in as-made form

Peak B decreases upon grinding, peak C1 show a slight increase. The most influenced one is C2 endotherm which decreases (samples 3 and 4) or disappears (samples 1 and 2).

Peak B has been attributed by Nagy *et al.* [8] to TPA species occupying the external shell of crystallites. This peak should increase then upon grinding, since the total surface of the crystallites increases. As can be seen on Fig. 2, the effect observed is quite opposite: peak B has decreased.

A possible explanation is as follows: the silicalite crystals obtained in alkaline conditions contain a large amount of SiOR defect groups (where R = alkali cations or TPA) in their structure [9]. The amount of defect groups can be as large as 32/u.c. in silicalite [9] corresponding to ca. 8 missing tetrahedral sites [10]. 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.

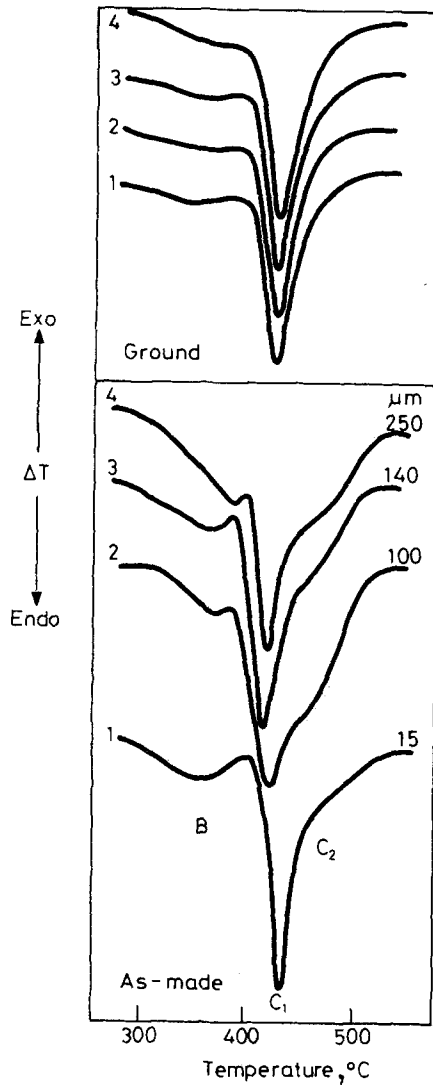


Fig. 2 DTA curves of large crystal silicalites in as-made form and upon grinding

The slight increase of C1 endotherm which is attributed to TPA⁺ ions neutralizing the inner SiO⁻ defect groups, can be explained by the easier decomposition of these species as well as the easier elimination of the decomposition products. In the case of initial large crystals, the decomposition products are not easily eliminated and the intensity of peak C2 is rather high. The larger are the crystals, the more intensive is this peak (Fig. 2). After grinding peak C2 decreases, and the remaining contribution can now essentially be attributed to the decomposition of more relaxed TPA species occurring at higher temperature. This effect can be seen for samples 2-4.

Sample 1 of smallest crystals investigated contains probably much less defect than the other samples 2-4. Hence its C1 endotherm is at the highest temperature and decreases after grinding.

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Zusammenfassung — Die thermische Zersetzung von Silikalit-1 Kristallen verschiedener Größe wurde untersucht. Es wurden ursprüngliche als auch zerkleinerte Kristalle einbezogen. DTA- und DTG-Kurven zeigen für die einzelnen TPA Spezies in den unzerkleinerten Kristallen verschiedene Zersetzungstemperaturen. Diese Unterschiede werden jedoch durch die Zerkleinerung beseitigt. Eine Erklärung für diese Erscheinung wird gegeben.