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THERMAL DECOMPOSITION OF TETRAPROPYLAMMONIUM IONS PROGRESSIVELY INCORPORATED INTO ZSM-5 FRAMEWORK DURING CRYSTALLIZATION

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ABSTRACT

The thermal decomposition of tetrapropylammonium (TPA) ions incorporated in the channel system of various (M)ZSM-5 zeolites progressively crystallized from [$zM_2O, Al_2O_3, 60SiO_2$] hydrogels (z=0.25,1 or 2;M=Li,Na,K,Rb,Cs) was investigated. Specific DTA endotherms allowed to differentiate TPAOH entities entrapped in Si-rich zeolitic frameworks and TPA^+ counterions to lattice Al-negative centers. The variation of the relative concentration of these species as a function of ZSM-5 particle growth could be related to the mechanism that governs that type of ZSM-5 synthesis. The existence of an Al gradient in the growing crystallites was confirmed.

INTRODUCTION

ZSM-5 is usually formed by hydrothermal heating of aluminosilicate hydrogels containing alkali cations and a specific structure-directing organic agent, usually tetrapropylammonium (TPA) ions (see e.g. ref. 1 as a recent review paper).

Very recently, we have reported a series of new data dealing with the thermal stability of TPA^+ ions occluded in various (Si,Al,alkali) hydrogels or incorporated in the corresponding final crystalline (M)ZSM-5 phases (2-5). DTA has shown that the latter species are very stable and can be of two types : ionic TPA^+ counterions to the framework negative charges, that are decomposed in the 450-480 temperature range, and less strongly bound TPAOH entities, released below 440°C (2,3). These observations are in agreement with other recent data (6,7).

As a contribution to a better understanding of the structural changes that undergo the various TPA-aluminosilicate associations during the hydrothermal transformation of the hydrogel into crystalline ZSM-5 zeolite, we describe, in the present paper, the thermal stability of TPA entities progressively incorporated in the framework of various (M)ZSM-5 zeolites during the synthesis process.

EXPERIMENTAL

A series of hydrogels having the general molar composition x TPABr - y $(TPA)_2O$ z M_2O - Al_2O_3 - 60 SiO_2 - 700 H_2O, where M = Li,Na,K,Rb and Cs; x + 2y = 8; y + z = 2 and z = 0.25,1 or 2, prepared under specific conditions (2-4), were left to crystallize at 165°C in Teflon autoclaves. The syntheses were interrupted after 3h, 6h, 9h and 24h heating and part of the corresponding intermediate phases so formed (gel + zeolite) removed, washed and dried. After determination of their degree of

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crystallinity by X-ray diffraction powder method, the amorphous gel was completely separated form the crystalline (M,TPA)ZSM-5 by the so called sonication method (3). Sample weight losses (TG-DTG) and thermal effects (DTA) were recorded by heating the dry zeolites in the range 20-600°C, under dry N_2 flow, at a rate of $10°C.min^{-1}$ in a STA-780 Thermal Analyzer from Stanton Redcroft. The detailed operatory conditions are described elsewhere (8).

RESULTS AND DISCUSSION

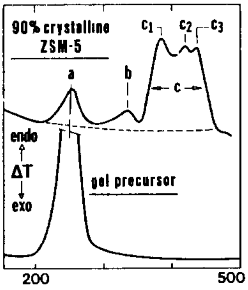

fig 1

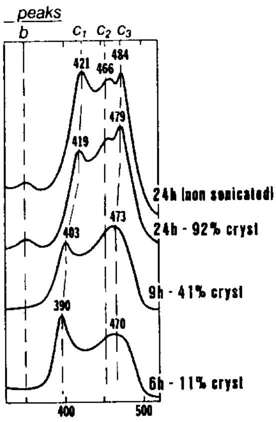

fig 2

Figure 1 illustrates the DTA endotherms that characterize the thermal decomposition of TPA units occluded in a typical [Na_2O - Al_2O_3 - $60SiO_2$] hydrogel precursor, and in the corresponding final crystalline (Na)ZSM-5. In the latter case, three main peaks are observed (a,b and c) as indicated in fig. 1, while only the peak a appears near 260°C in the hydrogel. This peak was shown to characterize the decomposition of monomeric and clathrated TPA^+ ions in interaction with the Al-negative centers of the gel (5). The DTA peak b was attributed to the decomposition of TPA^+ ions located at the external surface of the zeolite particles, but also partly extending into the channel system (2,3). The peak c shows a more complex shape that strongly depends on the nature and concentration of the alkali counterion (M^+) in the zeolite, as well as on the relative M/Al framework ratios (2). Figure 2 shows the variation of the relative intensities and the temperatures characterizing the different maxima belonging to peak c, recorded for intermediate and final phases obtained after progressive heating of a gel having the initial molar composition [0.25 Na_2O - Al_2O_3 - 60 SiO_2 - 8 TPA - 600 H_2O]. For each phase, the accompanying gel not yet transformed into ZSM-5 was removed by sonication so that the DTA endotherms exclusively characterize the various TPA species occluded in the crystalline ZSM-5 already formed but having not necessarily achieved its complete growth. For the ZSM-5 formed after 24 h heating, peak c is found split into three components (c_1, c_2 and c_3), while only c_1 and c_2 are observed for ZSM-5 having had their growth interrupted in the earlier synthesis stages (fig. 2).

Figure 3 gives the variation of the DTA temperature maxima Tc_1 and Tc_3 for the Li,Na,K and Rb systems, where M/Al = 2, as a function of % of crystallinity

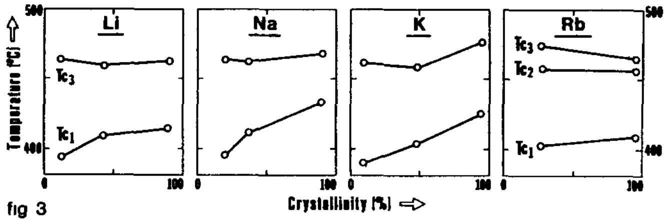

fig 3

of an intermediate (gel + zeolite) phase. It is observed that Tc_1 increases as a function of synthesis time, markedly for the Li,Na and K bearing zeolites, more slightly for Rb and Cs (not shown) systems. Conversely,Tc_3 remains fairly constant for the whole series (fig. 3), and only slightly increases when the concentration in alkali cation is low (systems where $M/Al = 0.25$ - fig. 2).

The relative intensities and positions of these peaks can be explained in the light of the crystallization model proposed for that particular type of preparation of ZSM-5 (1) : In the early stages of the synthesis, ZSM-5 grows by incorporating preferentially Si-rich species while Al-richer aluminosilicate entities are incorporated into the zeolite lattice only at the end of the crystallization process. This implies that the intermediate ZSM-5 crystals formed after only 6h or 9h heating exhibit essentially a Si-rich framework, while the final crystallites will show an Al-enriched outer rim. The presence of such an Al gradient was confirmed in the present case by analysis of surface (XPS) and bulk (EDX) Si/Al ratios in the various (M)ZSM-5 crystallites (5). The increase of Tc_1 is consistant with the model involving an increasing radial concentration in ZSM-5 particles during their growth. The decomposition products resulting from the Hoffman degradation of TPAOH located in a Si-rich phase, namely propylene and various (poly) propylamines (7), interact more readily with the Al surface species that are accumulated in the outer layers of the growing crystallite, so that their release is retarded.

As earlier suggested, the portion of peak c occurring above 440°C (which essentially contains c_3) can be a more extended measure of the amount of TPA^+ counterions to Al negative centers, while the portion occurring below 440°C better characterizes loosely bound TPAOH entities (2).

The relative increase of the intensity of c_1 (fig. 2), or of the DTA portion measured above 440°C (DTA > 440, fig. 4), as a function of crystallization time illustrates well the presence of predominant TPAOH species in an early formed Si-rich zeolitic phase, and their progressive transformation into TPA^+ counterions as the overall Al concentration in the crystals increases. TG data have confirmed indeed that the total amount of ($TPAOH + TPA^+$) per unit cell of ZSM-5 stays essentially constant during the growth process (5).

If the residual gel is not separated from the end-crystalline ZSM-5 phases

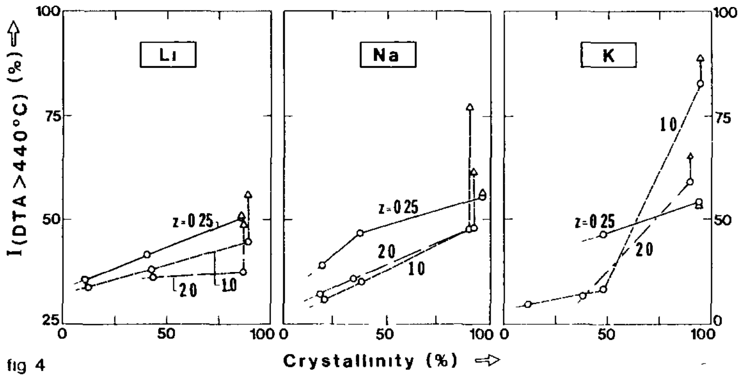

fig 4

by sonication, the corresponding intensity of DTA > 440°C is markedly larger (fig. 4, triangles) with respect to samples freed from the amorphous phase (fig. 4 - circles). This clearly illustrates the difficulty for the TPA (or for its decomposition products) to escape from a crystallite that is superficially covered by an Al-rich gel phase.

A third peak, c_2, appears at the end of the crystallization in the case of smaller cations (Li,Na,K), while it is present in all the intermediate phases containing Rb and Cs (fig. 2 and 3). This peak is tentatively attributed to TPAOH species that interact indirectly with negative Al centers, which are neutralized by alkali cations. This study is developed in more detail elsewhere (5).

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