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A comprehensive thermal study of the state of tetrapropylammonium (TPA) phase in ZSM-5

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Abstract

A thermal investigation of the decomposition of tetrapropylammonium (TPA) has led to a better insight into its state in the zeolite ZSM-5. DTA has shown an exothermic transition at $T_c = 753$ K. TPA salts decompose normally with endothermic transitions at lower T_c. TPA decomposes to give a proton at the zeolite framework. The affinity of the anionic framework for the resultant proton is so great that this exothermic peak could be assigned to a Brønsted site ≡SiO–H bond formation. Various thermodynamic parameters consistently reveal that a high population of TPA leads to a disordered structure. In effect, a progressive loss of TPA modifies the structure into a more ordered phase, which finds supporting evidence from X-ray diffraction studies. The enthalpy, entropy and activation energy of the transition show dependence on the TPA content of the zeolite. Apart from the thermal decomposition, gamma-rays have been found to induce another mechanism of decomposition that could lead to lattice defects of Lewis acid nature.

INTRODUCTION

Zeolites are usually synthesized from homogenized alkaline solutions of silica and alumina with different Si/Al ratios [1–3]. Inclusion in the synthesis mixture of various quaternary salts, particularly bulky alkylammonium cations, has introduced a new structure-directing parameter [4] into the synthesis mechanism, so that new type zeolites [5–8] have been patented to widen up the scope of zeolite chemistry and applications. Among the very recent interesting zeolites synthesized using such quaternary salts as templating agents are ZSM-5 [9], ZSM-11 [10] and their analogous pure silicalites [11,12]. In an excellent review, Lok et al. [13] have analysed the structure-directing features of these organic templates. The successful

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synthesis of ZSM-5 in the complete absence of such templating agents [14,15] has challenged the template theory emphasized in that review. However, the presence of quaternary salts, particularly tetrapropylammonium cations TPA^+, has no doubt had a great influence on the phase purity, crystallinity and stability of ZSM-5 [16,17].

In a recent thermal study of TPA decomposition in ZSM-5, Nastro et al. [18] have investigated occlusion-induced variations of TPA, with reference to the decomposition of pure TPA^+Br^-. They concluded a higher thermal stability for the occluded phase, which is explicit in a temperature rise of 170 ± 25 K for the dominant endothermic peak at 550 K, even for a physisorbed phase. In a more recent infrared study of the TPA phase in ZSM-5 [19], the formation of Brønsted sites has been found to be the direct result of its thermal decomposition, which should not happen unless TPA exists in the form of cations for neutralizing the anionic framework's aluminium sites. Physisorbed [18] and chemisorbed [19] phases would confirm the two possible mechanisms of TPA occlusion. Perhaps the former dominates for zeolites approaching Al-free silicalite whereas the latter dominates for zeolites of higher aluminium contents. The decomposition of TPA into Brønsted sites could proceed according to Hofmann degradation reactions [20].

The aim of the present investigation was to achieve a better insight into the state of the TPA phase in ZSM-5. This incorporates a discussion of the effects of varying the percentage occlusion and of gamma-irradiation on the thermal stability and other thermodynamic parameters of TPA, with reference to pure TPA^+Br^-.

EXPERIMENTAL

Materials

ZSM-5 was synthesized following the methods of Argauer and Landolt [9], with the intention of incorporating boron at increased levels [19] at the expense of zeolite aluminium content. Three zeolite batches with 0.47, 0.50 and 0.65 B–Al ratios were selected for this type of study. They were found

TABLE 1

Zeolite elemental analysis in terms of atoms per unit cell

Zeolite	Si	Al	B	B–Al ratio
TPA ZSM_1-5	91.9	2.8	1.3	0.47
TPA ZSM_2-5	91.2	3.2	1.6	0.50
TPA ZSM_3-5	91.7	2.6	1.7	0.65

to possess TPA^+ contents increasing with the B–Al ratio. The results of elemental analysis (Table 1) are reported as atoms per zeolite unit cell $[M_x(Al + B)_xSi_{96-x}O_{192}]$. TPA^+Br^- was prepared in a pure state by reacting *n*-propyl bromide with tripropylamine, both from Fluka Chemie AG.

Methods and equipment

The differential thermal analysis (DTA) of the products of TPA decomposition in ZSM-5 was carried out for zeolites weighing typically 3 mg. The measurements were performed using a Shimadzu DSC TA 30 thermal analyser in the range 300–900 K, with the temperature rising at a rate of 10 K min^{-1}. Comparison of these data with those for the decomposition of TPABr was carried out for a sample weighing 12 mg.

The effect of gamma-irradiation on the TPA phase stability in ZSM-5 was also studied by exposing the zeolite to gamma-radiation in air at 300 K at a dose rate of 1.45 MRad h^{-1} to give integrated doses of 1, 10 and 100 MRad. A ^{60}Co gamma cell 220 manufactured by Atomic Energy of Canada Ltd. was used for the irradiation.

The thermal data were treated as described previously [21].

RESULTS AND DISCUSSION

In agreement with the work of Nastro et al. [18], the thermogram of TPABr decomposition (Fig. 1(A)) shows two endothermic transitions: the former is evident in a weak peak at 400 K, being attributed to a solid phase transition, and the latter is dominant at 550 K, being associated with the decomposition. At variance with the cited report [18], the present data of TPA ZSM-5 decomposition (Fig. 1(B)) reveal so intense an exothermic transition at 753 K that appropriate sampling was difficult unless quite low masses of ca. 3 mg were used. In the vicinity of this temperature, Nastro et al. have reported no indication of a counterpart exothermic transition, even though they used a significantly larger mass of 100 mg. Endothermic transitions at 695 and 745 K have rather been reported [18] to change intensity with the Si–Al ratio. The discrepancy could be associated with the zeolite Si–Al ratio, as Nastro et al. used higher ratios than that reported in the present work, and therefore they attributed the relevant endothermic peaks to the decomposition of a physisorbed TPA phase. Exothermic transitions are usually associated with bond formation. The exothermic transition revealed in this work (Fig. 1(B)) would therefore be tentatively assigned to Brønsted SiO–H bond formation, the direct result of chemisorbed TPA^+ decomposition. This could be true if one considers the T_c order. TPA decomposes first at a T_c of 550 K for TPABr or at 720 ± 25 K for the highly siliceous TPA ZSM-5 and silicalite. Owing to its high proton affinity, the anionic framework SiO^- coordinates so firmly to the

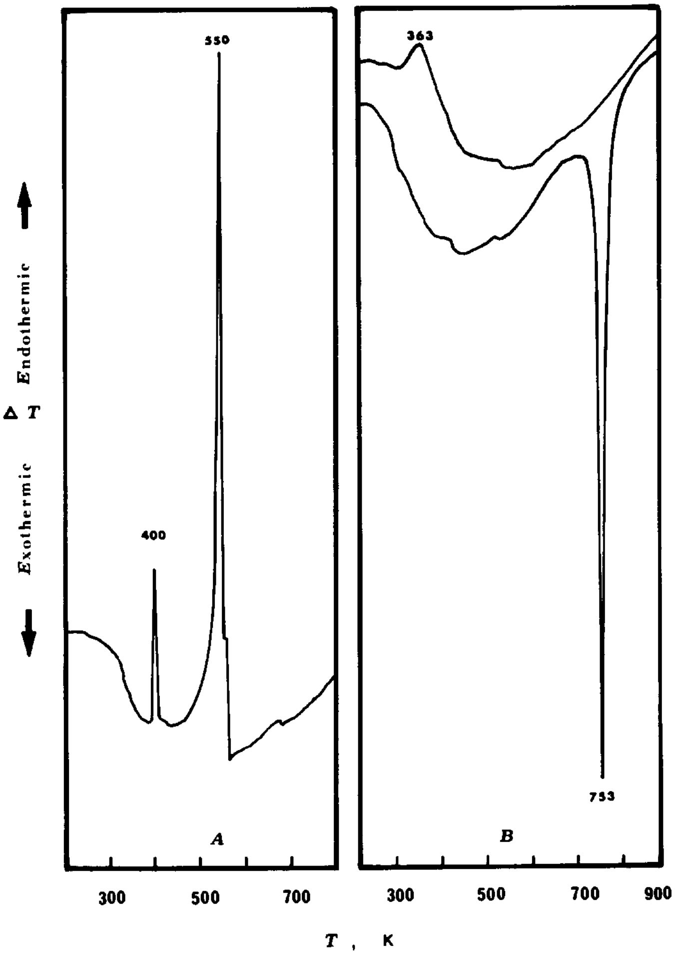

Fig. 1. Differential scanning thermogram of (A) TPABr; (b) TPA ZSM_3-5, as a fresh sample (lower curve) and after decomposition into HZSM-5 (top curve).

resultant proton that it releases considerable heat at 753 K. A confirmation of partial zeolite protonation stems from the appearance of a weak endothermic peak at 363 K (Fig. 1(B)) having no counterpart in the Na-form zeolite. This transition has recently been attributed to a phase transition in the H-form ZSM-5 [21].

Analysis of the specific heats of these endo- and exo-thermic transitions (Fig. 1) would illustrate the quite large difference between physical and chemical association of TPA with the zeolite structure. Chemical association involving protons leads to an almost fourfold greater C_p at the transition (Fig. 2(B)) than that (Fig. 2(A)) required for its decomposition, which would explain the origin of the exothermic transition. This is also reflected in the large difference in activation energy; this is 443 and 113 kJ g^{-1} for TPA ZSM_3-5 and TPABr respectively. The peak associated with

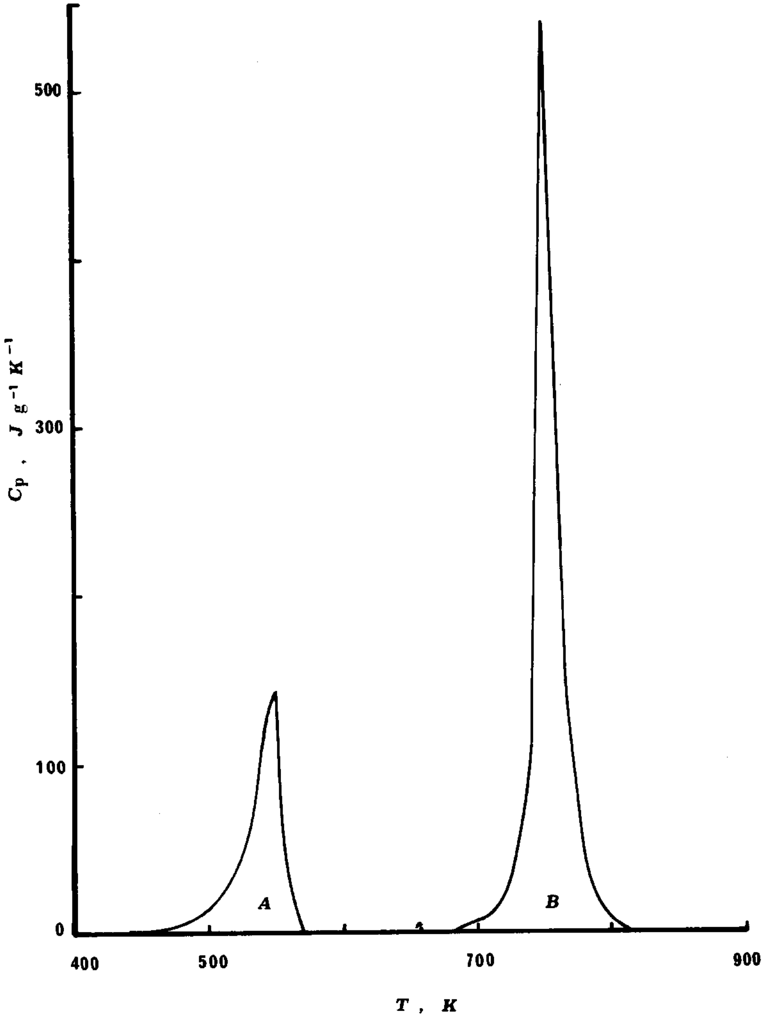

Fig. 2. The temperature dependence of the specific heat C_p for (A) TPABr; (B) TPA ZSM$_3$-5.

the exothermic transition is sensitive to variation of the zeolite TPA content. Both C_p (Fig. 3) and T_c (Table 2) of the transition rise in line with the TPA content. The extent of TPA occlusion appears to be a function (Fig. 3) of the zeolite boron–aluminium ratio. Incorporation of the smaller B and/or Si at the expense of the zeolite Al content appears to provide a relatively larger pore volume, which favours the probability of TPA occlusion.

Tight occlusion of TPA, even if it exists as a physisorbed phase in ZSM-5, should influence the structure. This is clearly evident (Fig. 4) in the large shift of the thermodynamic structure parameter α observed upon the occlusion. TPABr crystallizes in a tetragonal space group I_4^-, with cell

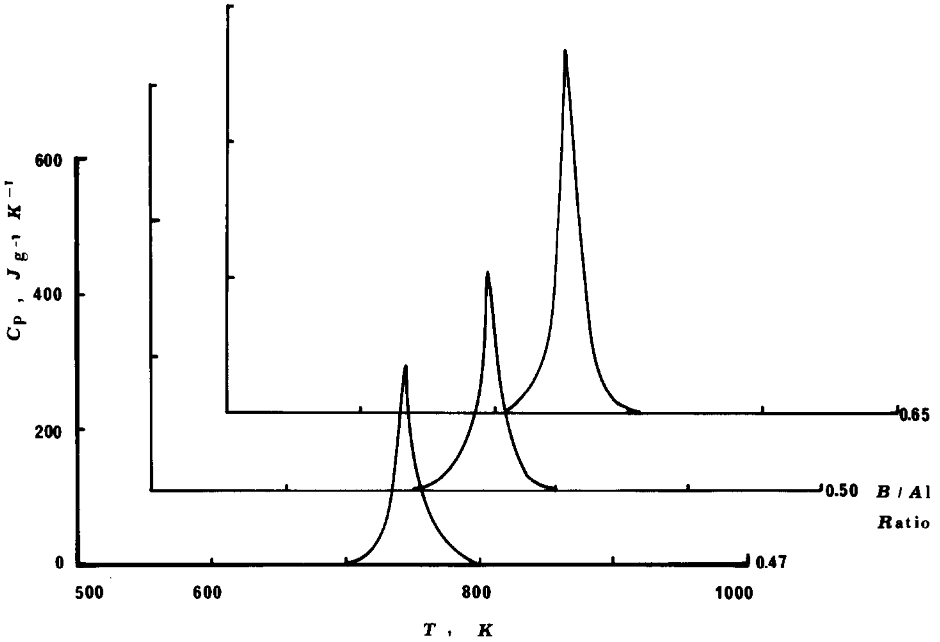

Fig. 3. Variation of the temperature dependent specific heat with the zeolite TPA content, estimated as a function of zeolite B–Al ratio.

constants $a = b = 8.24$ Å and $c = 10.92$ Å [22]. These dimensions fit tightly the intersection of the ZSM-5 channels, which would lead to the conclusion that four TPA species can be accommodated tightly at the four intersections of each zeolite unit cell. However, this process seems to involve a random distribution, which results in a disordered structure. The thermodynamic structure parameter α takes values below unity for an ordered structure, whereas higher values indicate random distribution [23]. Figure 4 reflects the state of TPA upon shifting from the ordered structure of TPABr with $\alpha = 0.69$ to the disordered structure of $\alpha = 1.33$ for the higher TPA zeolite sample, TPA ZSM$_3$-5. Other samples occluding lower amounts, namely TPA ZSM$_2$-5 and TPA ZSM$_1$-5, show lower values approaching the

TABLE 2

Dependence of the thermodynamic parameters on the TPA content [a]

Zeolite	T_c (K)	ΔH (J g^{-1})	ΔS (J g^{-1} K^{-1})	B–Al ratio
TPA ZSM$_3$-5	753	296.9	0.39	0.65
TPA ZSM$_2$-5	750	255.3	0.34	0.50
TPA ZSM$_1$-5	745	192.5	0.26	0.47
TPABr	550	88.9	0.16	

[a] Expressed in terms of zeolite B–Al ratio.

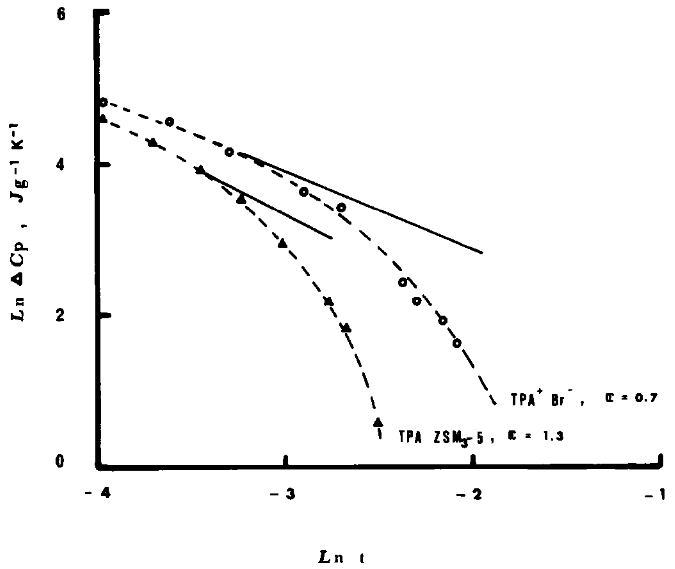

Fig. 4. Effect of chemisorbed occlusion on the structure of TPA compared with that of TPABr.

α value of TPABr. A direct measure of this disordered structure could be estimated from the entropy (Table 2) ΔS, the thermodynamic disorder parameter. Reducing the amount of TPA, as explicit in a reduced zeolite B–Al ratio, lowers ΔS to values approaching that of TPABr. TPA occlusion is well known to modify the ZSM-5 structure, as is shown by X-ray diffractometry [12].

Tight occlusion of TPA in ZSM-5 also modifies other thermodynamic parameters. This is clearly shown by the increased T_c (Table 2) of 200 K with respect to TPABr. As a result of modified thermal stability, the enthalpy change ΔH (Table 2) of the TPA decomposition into the zeolite Brønsted sites is also greater for the more occluded TPA sample. This demonstrates clearly the role of occlusion in enhancing the thermal stability of TPA, probably via chemisorption to the zeolite framework.

Apart from the thermally induced proton transfer by TPA, exposure of TPA ZSM-5 to gamma-rays appears to induce a different mechanism of TPA decomposition, which is demonstrated (Fig. 5) for TPA ZSM$_3$-5. The exothermic transition shifts to lower T_c and intensity as a result of the exposure. The exothermic transition in this case is therefore a function of the TPA remaining in the zeolite structure. The severe gamma-induced decomposition appears therefore not to yield the Brønsted sites afforded by the thermal decomposition, as is evident by the absence of the endothermic peak indicating the H-form zeolite at 363 K; compare the top thermograms of Figs. 5 and 1(B). The severe irradiation might result, rather, in lattice defects of Lewis acid nature, similar to that obtained by surface

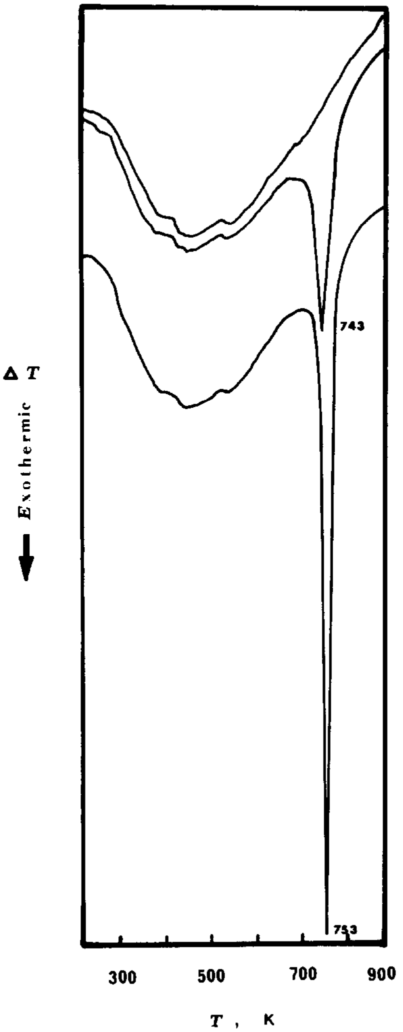

Fig. 5. Gamma-induced shift in both the peak intensity and T_c of the exothermic transition of TPA ZSM$_3$-5. Fresh sample (bottom), exposed to 10 MRad (middle) and to severe gamma doses (top).

dehydroxylation [24]. Such defects have recently been reported [25] to enhance the electrical and conductivity of this typical zeolite. The number of defects is calculated [25] from the relation

$$\ln \Delta C_p T^2 = \ln(ZNU^2/R) - U/RT$$

where Z is the coordination number of TPA, U is the activation energy, R is the universal gas constant and N is the number of defects.

The gamma-induced loss of the temperature dependent C_p at the exothermic transition is clearly shown (Fig. 6) to correlate with the gamma dose. Complete disappearance of the associated peak (Fig. 5, top) results at

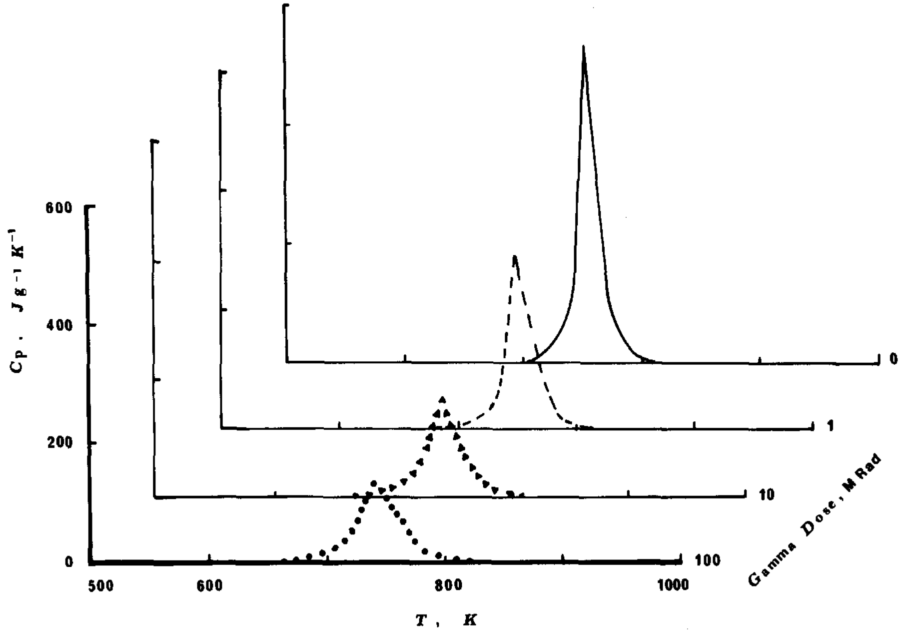

Fig. 6. Three-dimensional representation of C_p–temperature–gamma dose.

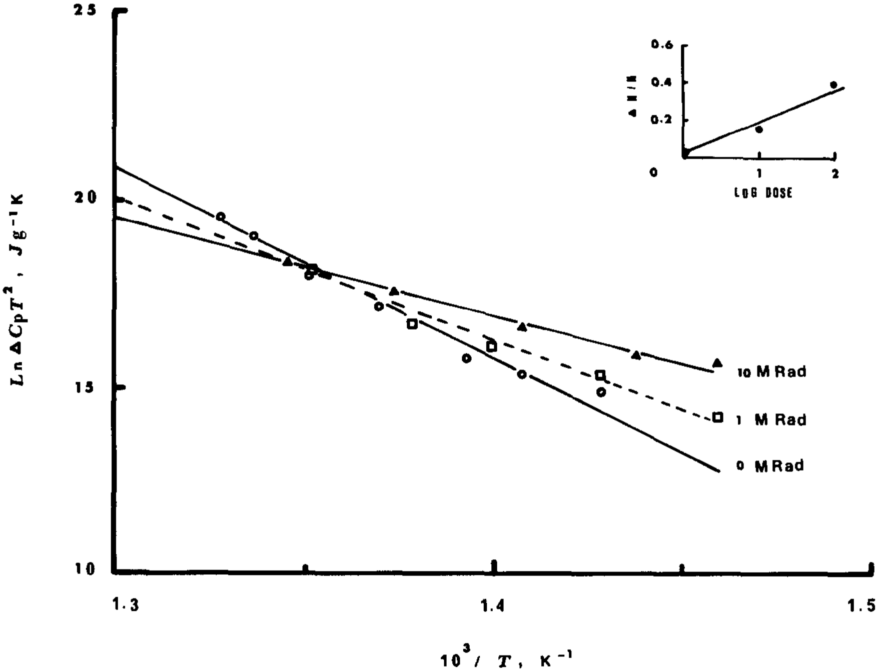

Fig. 7. Dependence of gamma-induced shifts of both the derived activation energy and the relative change of number of defects.

TABLE 3

Gamma-induced shifts in the thermodynamic parameters of TPA ZSM_3-5

Gamma dose (MRad)	α	T_c (K)	ΔH ($J\,g^{-1}$)	ΔS ($J\,g^{-1}\,K^{-1}$)	U ($kJ\,g^{-1}$)
0	1.33	753	296.9	0.39	443.2
1	1.05	748	267.0	0.36	332.4
10	0.94	743	191.7	0.26	174.5
100	0.33	740	173.4	0.23	160.7

doses higher than 100 MRad. The activation energy decreases with increased gamma dose, as is evident from the lowered slope of the linear dependence (Fig. 7), which would confirm the role of gamma-induced TPA decomposition in the zeolite structure. As it has been mentioned that the T_c of the thermal decomposition is a function of the TPA content (Table 2); the drop in T_c with irradiation (Table 3) supports the conclusion that gamma-rays participate in the decomposition, and this is also shown by the changes of both enthalpy and entropy (Table 3). Increased gamma participation in TPA decomposition should leave an increased number of structure defects. This is certainly true, as the relative change of the crystal defects follows a linear dependence (Fig. 7, top) on the logarithmic values of the gamma doses.

Finally, despite the crystal defects caused by the gamma-irradiation, the lowered population of TPA appears to have a better opportunity of a more ordered structure. This is clearly shown from the thermodynamic structure parameter α (Table 3), which shifts to lower values with increasing gamma dose.

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