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Structural interpretation of the ambiguous loopy effect of gamma irradiation on the phase transition thermodynamics of US-HY zeolite

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Abstract

US-HY zeolite appears to show a topotactic phase transition at 388 K which is susceptible to interaction of the surface silanols with sorbed water and is sensitive to escalated doses of gamma irradiation. This work proposes a structural interpretation for the strange parabolic dependence of the thermodynamic parameters C_p, ΔH and U of the transition on the irradiation dose; they show consistently a minimum at 20 Mrad. The 3-dimensional Ising model of the phase transition is apparently insensitive to the irradiation, which precludes the direct role of gamma irradiation in modifying the zeolite symmetry by the formation of lattice defects. The primary reduction of the thermodynamic parameters below 20 Mrad is attributed to increased lattice flexibility. Interaction of sorbed water with gamma-induced mobile protons assists in permitting symmetry shifts of the lattice at lower activation energies. Excessive doses of gamma irradiation, however, may cancel the former effect by either proton trapping or surface dehydroxylation, which might explain the subsequent rise of the thermodynamic parameters above 20 Mrad. This interpretation is supported by data manipulation of the consistent shifts in the IR band absorbance and band width of the vibrations of the zeolite framework.

INTRODUCTION

Ultrastable (US)-HY zeolite enjoys academic and industrial interest because of its important features and widespread applications [1–5]. Partial dealumination of the zeolite lattice, although it reduces the average number of acidic sites, provides the zeolite with stronger acidity [6–9] and higher thermal stability [10–13]. Experience [14–24] has shown that different methods of dealumination yield zeolites with different features. One aspect that has long been debated is whether or not the dealuminated zeolite incorporates nest silanols as lattice defects, created at vacancies in the framework aluminum. High temperature treatments such as steaming or reaction with $SiCl_4$ vapor have shown evidence of unit-cell contraction [12–18], as an indication of silicon replacing aluminum in the zeolitic lattice.

However, mild temperature treatments with HCl or EDTA [19–24] revealed incorporation of the nest silanols. It appears that nest silanols form in all cases [25], but they undergo a thermal dehydroxylation under more severe pretreatment conditions. The acidity and activity of such nest silanols [26–28] have been previously characterized.

Zeolites undergo topotactic transformations at the dehydration temperature [29–31], where interaction of sorbed water with the surface silanols plays a major role in assisting the lattice flexibility [32, 33]. Recently [34], the role of sorbed water, Brønsted sites, zeolite dealumination and gamma irradiation in modifying the phase transition of ZSM-5 has been demonstrated. In a more recent report [35], unlike the thermal decomposition of ZSM-5-occluded TPA cations into zeolite Brønsted sites, gamma irradiation, rather, induced decomposition into Lewis sites, which influence the transition differently. Gamma irradiation has also been reported [36] to enhance the proton mobility.

The aim of this work is to provide a structural interpretation that may help in understanding the observed ambiguous parabolic dependence of the C_p, ΔH and U values of the transition on the dose of gamma irradiation.

EXPERIMENTAL

The material used for catalysis was US-HY zeolite (BDH Ltd., UK). The sample purity and crystallinity were confirmed by their sharp XRD and IR spectral patterns. Analysis by ICP-AA and XRF spectroscopy revealed a consistent unit-cell composition of $H_{13}Al_{13}Si_{179}O_{384}$ with an Si/Al ratio of approx. 14. Analysis by TG, however, showed a much higher population of surface silanols than that formulated as being associated with the zeolite aluminum. Surface silanols dehydroxylated at 823 K were counted as 60 H per unit cell, i.e. an average of approx. 12 nests are expected to occupy each unit cell. Such a high population could be considered as contributing to the modified electrical conductivity [36] and the thermal properties observed in the present study.

Different zeolite samples were exposed to integrated doses of 5, 10, 15, 20, 30, 40, 50 and 100 Mrad of gamma rays. The irradiation was performed in air at 300 K, using a ^{60}Co gamma-cell 220 (Atomic Energy of Canada Ltd.). Differential thermal analysis was performed in air in the temperature range 288–1273 K, with a heating rate of 10 K min^{-1} for samples weighing 30 mg, using a Shimadzu DSC TA 30 Thermal Analyser. Infrared spectra were measured in the 1400–400 cm^{-1} region of the zeolite framework vibrations, using the KBr disk technique and a Nicolet 510 FT-IR spectrometer. These measurements were performed for precisely probing possible spectral and thermal shifts that might be induced by gamma irradiation.

RESULTS AND DISCUSSION

Various zeolites show evidence of solid state phase transitions. Some of these transitions are coincident with water desorption, and are therefore considered as water-assisted processes [34]. Such phase transitions can be investigated by thermal analysis and interpreted using the structure-probe technique of infrared spectroscopy.

Thermal analysis

US-HY yields a thermogram dominated by two endothermic transitions at 388 and 823 K, with the latter evidently attributed to surface de-

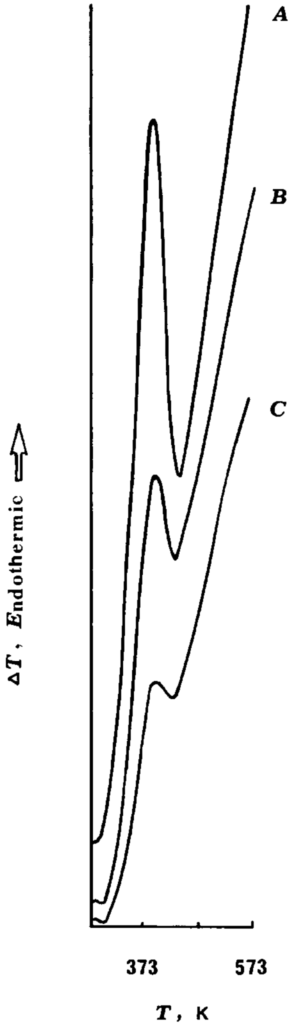

Fig. 1. Thermogram of US-HY zeolite: (A) not pre-treated, (B) after heating at $T \geqslant 623$ K and (C) as in (B) for a sample irradiated at 20 Mrad.

hydroxylation. Figure 1 illustrates the thermogram in the temperature range of the first transition, 273–573 K. The dominant contribution of this transition, see Fig. 1(A), is due to physisorbed water. Nevertheless, a significant part of the transition (Fig. 1(B)) persists for samples pretreated at $T \geqslant 623$ K, where desorption of physisorbed water, as evident from the thermogram, should be complete. This persistent part of the transition is sensitive to gamma irradiation, see Fig. 1(C). Both results suggest assignment of the persistent part to a solid state water-assisted phase transition, similar to that observed for HZSM-5 [34]. Because of the asymmetric appearance of Fig. 1(B), compared to Fig. 1(A) and considering the amount of physisorbed water as a common factor, data manipulation based on the hydrated samples is more appropriate for discussing the present thermodynamic data.

The transition specific heat capacity C_p decreases to a minimum (Fig. 2) at 20 Mrad. The C_p value of US-HY zeolite is twice that of HZSM-5. This, together with the higher T_c of the present zeolite, reflects the higher

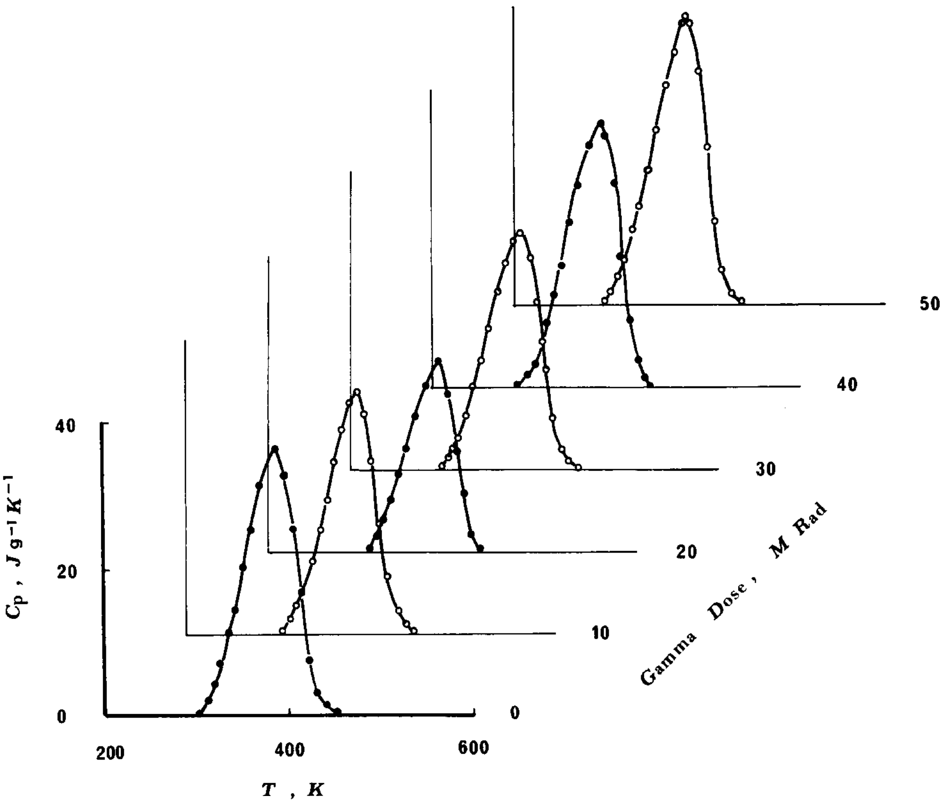

Fig. 2. Parabolic change of the phase transition temperature-dependent specific heat capacity C_p with the irradiation dose.

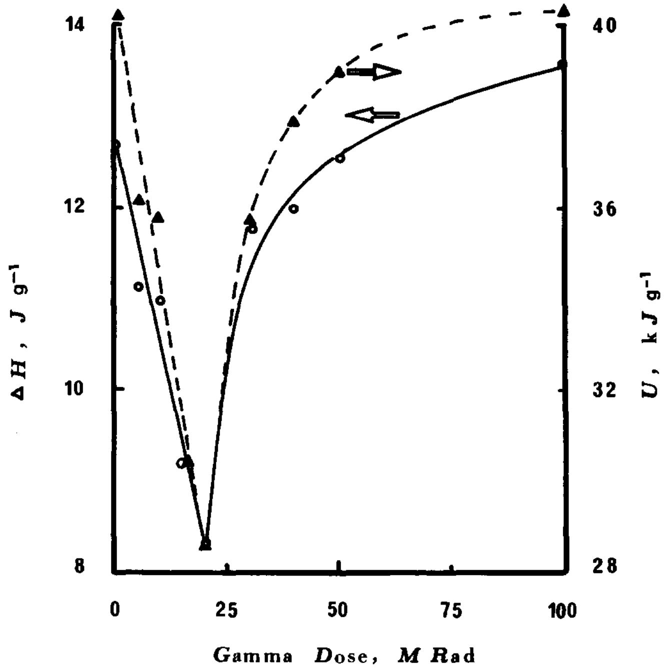

Fig. 3. Consistent parabolic dependence of (i) enthalpy change ΔH (—) and (ii) activation energy U (- - -), on the irradiation dose, indicating a minimum at 20 Mrad.

association of the nest silanols of US-HY. Evidence of such a strong association has been reported [37].

The enthalpy change ΔH (Fig. 3, solid line) is calculated with reference to that of pure indium at 703 K (28.4 J g^{-1}). It shows a minimum at 20 Mrad. The high-dose plateau above 50 Mrad indicates a saturation effect of the irradiation.

The activation energy U can be estimated from the logarithmic dependence [38] of the equation

$$C_p = (ZNU^2/RT^2)\,e^{-U/RT} \quad (1)$$

where Z is the coordination number, N the disorder number and R the gas constant. The plot in Fig. 3 (dashed line) shows a typical dependence of U on the irradiation dose with a minimum at 20 Mrad. These consistent data demonstrate a transition governed by two mechanisms conflicting at 20 Mrad. The maximum gamma-induced shift of the activation energy amounts to only 12 kJ g^{-1}, which assigns the data to interaction of the gamma rays with mobile protons rather than with the stationary lattice. This tentative assignment is supported by a further thermal parameter that identifies the model to which the transition belongs:

$$C_p = At^{-\alpha} \quad (2)$$

where α is a thermodynamic function of the transition model, A is a

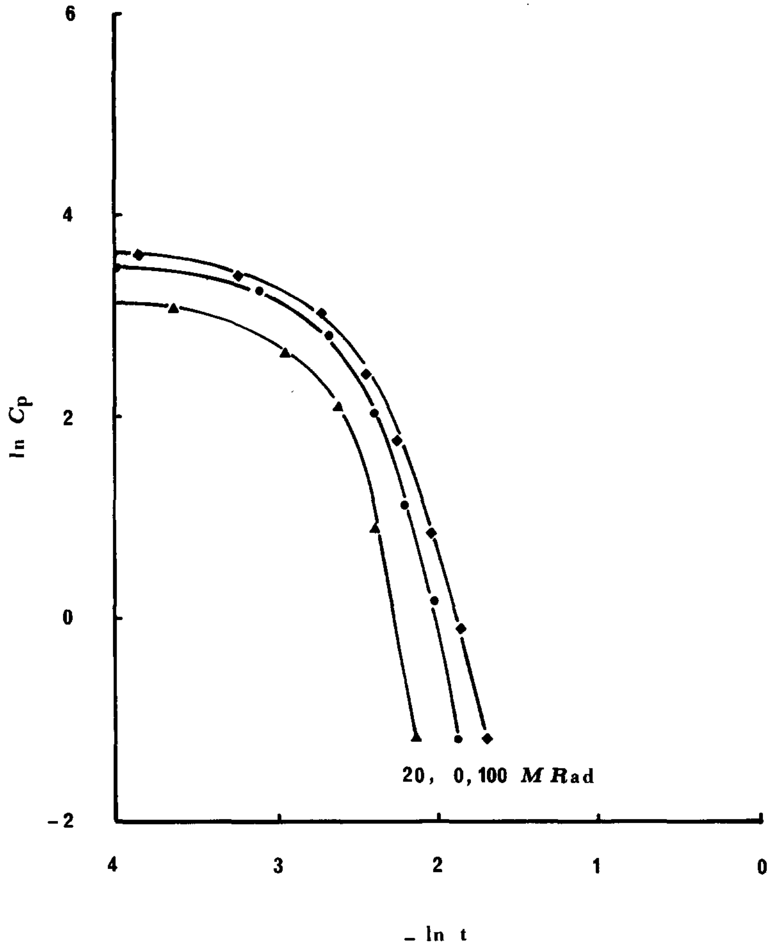

Fig. 4. Negative effect of gamma irradiation on the 3-dimensional Ising model of the transition, as evident in equal values of the critical exponent α.

constant and $t = (T - T_c)/T_c$. The critical exponent α is best determined near T_c [39]; its calculated value of 0.11 fits well [40] with the 3-dimensional Ising model and is insensitive (Fig. 4) to the irradiation. This would preclude a direct effect of the irradiation on the zeolite lattice.

In order to pinpoint the origin of the ambiguous shifts of the thermodynamic parameters, more crucial structural information are still required, in particular from the structure-probe technique of infrared spectroscopy.

Infrared spectral analysis

Figure 5 shows the IR spectrum of the zeolite lattice vibrations at the most discriminative irradiation doses. The spectrum is dominated by strong absorptions of the asymmetric stretching modes of the ≡Si–O–Al≡ skeletal

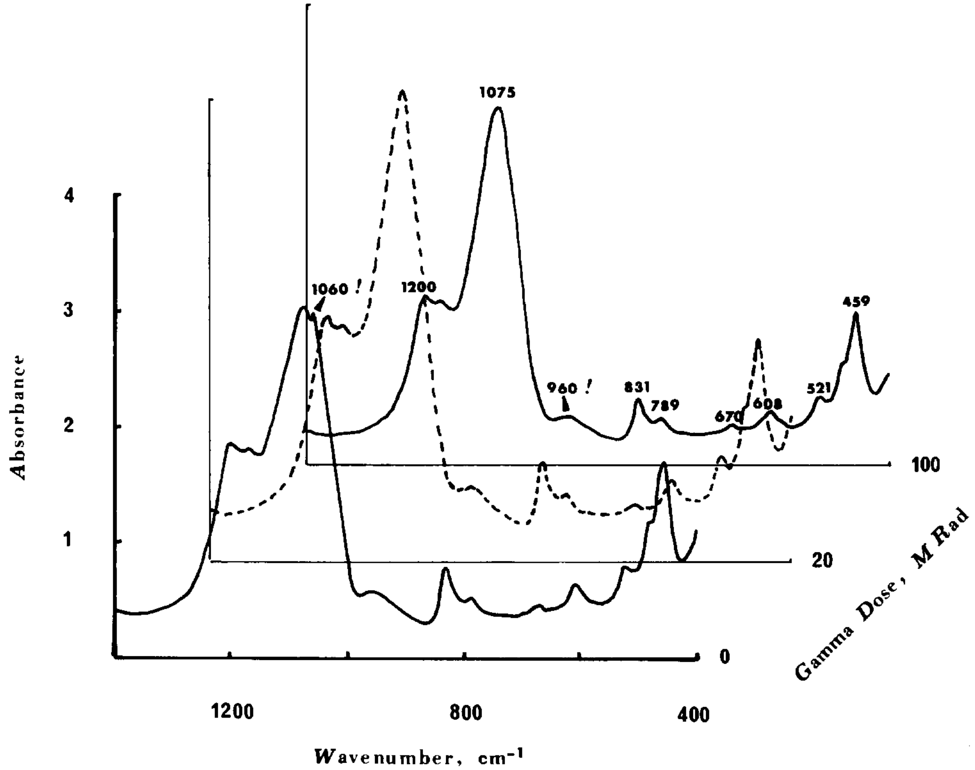

Fig. 5. Infrared spectrum of the zeolite lattice vibrations at the most discriminative irradiation doses.

vibrations at 1200 and 1075 cm^{-1}. Less dominant symmetric stretching modes appear at 670, 608, 521 and 459 cm^{-1}. In addition, two absorptions, which are not often observed, appear at 1060 and 960 cm^{-1}. The former band is often obscured by the strong absorption at 1075 cm^{-1}. In a very interesting report [41], neutron inelastic scattering spectra of NaHY zeolite showed strong evidence that the 1060 cm^{-1} band is due to the in-plane bending mode of the bridged [≡Si–O–Al≡]–H$^+$ silanols. Increased proton mobility assists in shifting this band to lower frequencies as a result of the reduced O–H bond force constant; this is evident [37] for the present zeolite.

Gamma irradiation induces significant shifts in the band width and absorbance (Fig. 5), rather than in the frequency, with the absorptions at 1200 and 1075 cm^{-1} being most influenced. For instance, the $\nu_{1/2}$ at 1075 cm^{-1} is reduced by 30 cm^{-1}. The band at 608 cm^{-1} is least sensitive to the irradiation and can, therefore, be considered as a reference band for absorbance normalization. It is interesting to observe a consistent rise (Fig. 6) of the band absorbance to a maximum at 20 Mrad. The rise below 20 Mrad may be associated with increased bond dipole forces which,

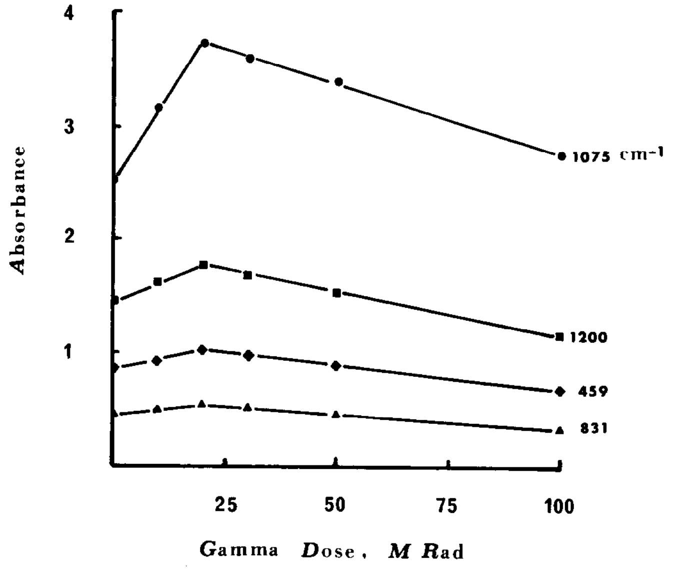

Fig. 6. Linear dependence of IR band absorbance of the zeolite framework vibrations on the irradiation dose, with a consistent maximum at 20 Mrad.

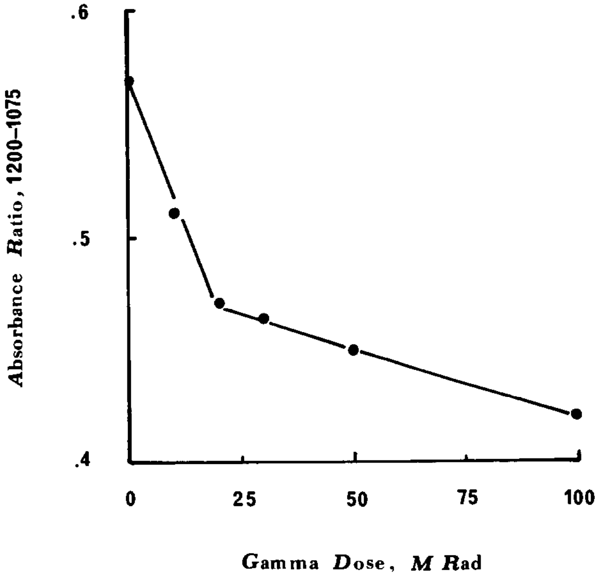

Fig. 7. Critical change of the linear dependence of the IR 1200–1075 band absorbance ratio on the irradiation dose at 20 Mrad.

together with the reduced $\nu_{1/2}$, can be a consequence of increased proton mobility. The subsequent loss past 20 Mrad is consequently attributed to an opposite effect, which can be severely gamma-induced surface dehydroxylation or proton trapping [42, 43].

In conclusion, gamma irradiation affects the zeolite lattice of US-HY indirectly by influencing the silanol mobility, rather than by creating lattice defects as normally observed. Lattice defects would broaden the IR bands rather than cause the spectral shifts observed in this study. Evidence of modified proton mobility can be seen in the band associated with the bridged silanols at 1075 cm^{-1}, which is most affected by the irradiation, see Fig. 6. The greater loss of the 1200/1075 band absorbance ratio below 20 Mrad, shown in a higher sloping linear dependence (Fig. 7), demonstrates the greater influence of gamma irradiation on the mode at 1075 cm^{-1}. The maximum rise of the spectral band absorbance and the maximum drop of the thermodynamic parameters at 20 Mrad should be attributed to a common contributer. This is most probably gamma-induced proton mobility which, together with sorbed water, modifies the zeolitic lattice towards a more accessible solid state topotactic phase transition.

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