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The contrasting effects of γ-irradiation on the lattice transition and NH_4^+ decomposition thermodynamics in NH_4X zeolite.
A DTA investigation

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Abstract

NaX zeolite shows a solid state phase transition at a T_c of 450 K, which undergoes a shift to 470 K upon exchange to NH_4X zeolite. The exchange also induces a broadening in the C_p band and a reduction in the C_p (at T_c), ΔH and $E^{\#}$ values. These opposing effects of increased cation mobility (exchange-induced lower C_p, ΔH and $E^{\#}$) and lattice association (exchange-induced higher T_c and C_p band width) are emphasized further when investigating the hysteresis effect of γ-irradiation on the thermodynamics of the more mobile NH_4X transitions. In contrast with γ-radiation-insensitive NaX, the thermodynamics of the NH_4X zeolite solid phase transition at 470 K and the NH_4 cation decomposition at 548 K undergo parabolic shifts of transition T_c, C_p and ΔH values, which are highly discriminated at 10 Mrad. Below this dose, the γ-rays induce a consistent drop in the C_p and ΔH values, a consistent rise in $E^{\#}$, and an inconsistent rise in the T_c of the NH_4 cation decomposition, and an inconsistent fall in the T_c of the zeolite lattice transition. All these shifts revert to normal at higher doses causing the hysteresis effect. Strong evidence indicates that γ-rays induce cation trapping and, therefore, also lattice defects because cation mobility is enhanced; both effects are considered to cause both the mutually opposing thermodynamics and the hysteresis effect observed following the irradiation.

INTRODUCTION

In a recent investigation [1], a thermal analysis of the solid-state phase transition of US-HY zeolite revealed a strange parabolic dependence of the lattice phase transition thermodynamics on the dose of γ-irradiation received. The dependence of the transition C_p, ΔH and $E^{\#}$ values pointed to a minimum at 20 Mrad. Interpretation of this strange dependence was attributed to γ-radiation-enhanced mobility of the zeolite Brønsted sites, which, below 20 Mrad, enhances the flexibility of the lattice, and, therefore, assists the shift in framework symmetry, particularly if aided by sorbed water. The subsequent rise in transition thermodynamics above 20 Mrad was, therefore, attributed to a decrease in the lattice freedom because of either proton trapping or surface dehydroxylation. This interpretation was founded on spectral observation rather than straightforward thermal evidence. The lattice vibrations, particularly those associated with the zeolite Brønsted site, showed a rise in IR absorptivity, reaching a maximum at 20 Mrad. Enhancing the proton mobility, at low irradiation doses, raises the lattice bond dipole (increased IR absorptivity) and assists in permitting a symmetry shift of the zeolite framework at lower energies.

In contrast with the phase transition of US-HY zeolite at a T_c of 388 K, which is complicated by the thermodynamics of water sorption, NaX zeolite shows a solid-state phase transition at a higher T_c of 450 K, where the contribution of sorbed water should be minimal. Also, in addition to the lattice transition at a T_c of 470 K, NH_4X zeolite shows a decomposition transition of NH_4^+ at a T_c of 548 K. Manipulation of the thermodynamics of both the lattice and NH_4^+ decomposition transitions would provide a better way to explore the origin of the hysteresis effect of the irradiation on the thermodynamics of the present zeolite.

EXPERIMENTAL

The solid materials under investigation were the Na and NH_4 forms of 13X zeolite, BDH Chemicals Ltd. Poole England, which were manufactured by Linde Air Products Company, a Division of Union Carbide and Carbon Corporation.

Different zeolite samples of both zeolite forms were irradiated with increasing doses of γ-radiation, namely 5, 10, 20, 30 and steps of 10 Mrad up to 100 Mrad. 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 300–800 K for samples weighing 30 mg, using a heating rate of 10 K min^{-1} and a Shimadzu DSC TA 30 thermal analyser.

The DTA data were treated as described previously [1–3].

RESULTS AND DISCUSSION

A general assessment of the DTA thermogram shows an endothermic solid-state phase transition at T_c of 450 K for NaX zeolite. In addition to the endothermic NH_4^+ decomposition transition at a T_c of 548 K [4], a solid-state transition is shown at a T_c of 470 K for NH_4X zeolite. Measurements at elevated temperatures confirm this assignment. The NH_4^+ band contributes to the thermogram up to 673 K, above which the thermogram is dominated by the zeolite phase transition alone. The zeolite structure collapses above 1203 K for the Na-form and at lower temperatures (dependent on the

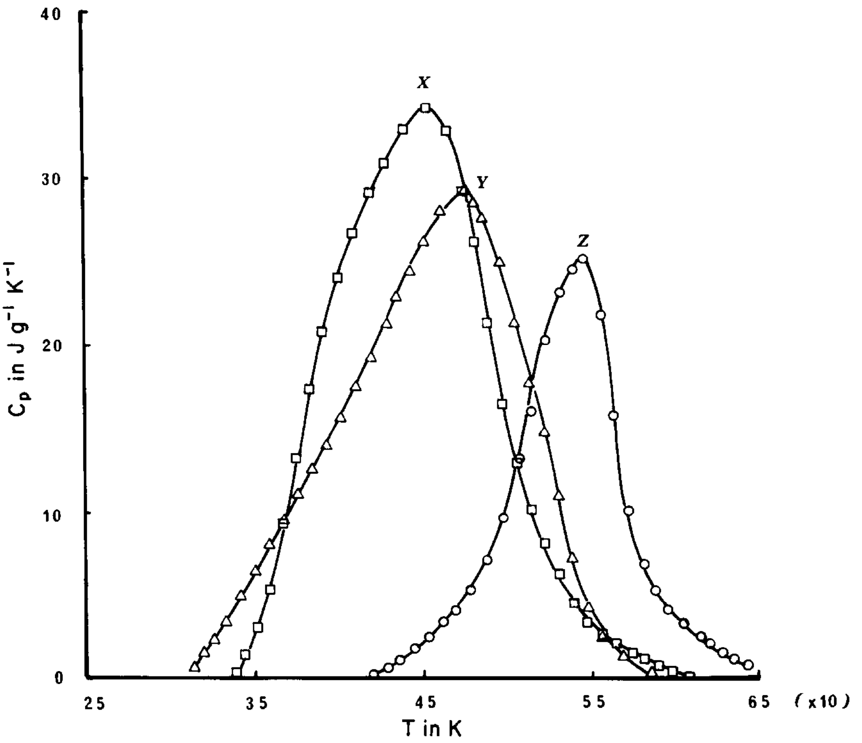

Fig. 1. Dependence of C_p on T for the lattice transition of NaX (X) and MH$_4$X (Y) zeolites and for the NH$_4^+$ decomposition (Z).

exchange extent) for the less thermally stable NH$_4$-form zeolite. The scope of the thermal investigation will therefore be limited to the temperature range of 300–800 K. Assignment of the solid-state transition conforms with previous results [5–9] for the cation- and water-induced lower symmetry of the zeolite framework, which can be modified upon desorption or cation exchange.

Figure 1 correlates the C_p values for the lattice transition of the Na-form (X) and NH$_4$-form (Y) zeolites. Exchange into the latter form reduces the transition C_p at the T_c. Because NH$_4^+$ is more mobile than Na$^+$, the exchanged cations assist the lattice mobility towards symmetry shifts at lower energies [5–7]. The exchange also results in an increase in both the transition T_c and C_p band width, both being indications of increased lattice association. Figure 1 also includes the C_p dependence for the zeolite deammoniation process (Z). Including the thermodynamics of this NH$_4^+$ decomposition in the discussion, however inappropriate it may seem to correlate the thermodynamics of a shift in physical symmetry with a real chemical reaction, helps in exploring the origin of the ambiguous hysteresis effect of γ-irradiation which is observed in both the previous report [1] and this study.

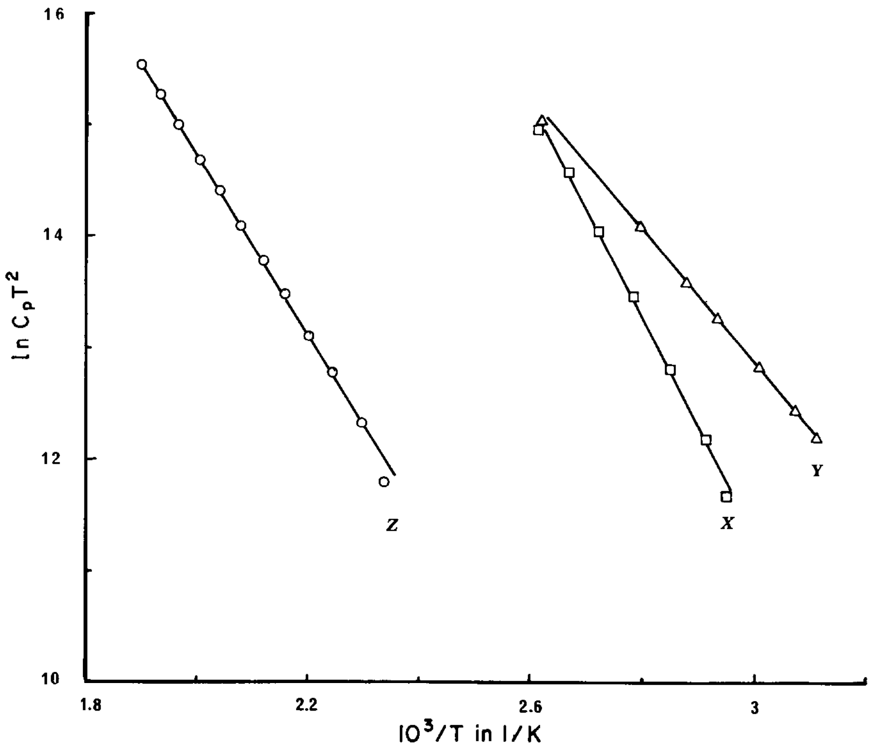

Fig. 2. Arrhenius-like dependence of C_p on T (eqn. (1)) for estimation of the activation energy of Nax (X) and NH_4X (Y) lattice transitions and of NH_4^+ decomposition (Z).

The activation energy of the transition $E^{\neq}$ is calculated [10] from the Arrhenius-like dependence of eqn. (1)

$$\ln C_pT^2 = \ln(ZNE^{\neq 2}/R) - E^{\neq}/RT \qquad (1)$$

where Z is the coordination number, N the lattice defects, and R the universal gas constant.

It is clear that the exchange lowers the activation energy of NaX (Fig. 2, curve X) from 79.8 to 48.2 kJ g^{-1} of NH_4X (Fig. 2, curve Y), probably because of the enhanced mobility. The intermediate value of 67.3 kJ g^{-1} of the NH_4^+ decomposition (Fig. 2 curve Z) is in fact extremely high if measured in kJ mol^{-1}, as compared with the much lower lattice energy measured in kJ per unit cell. This emphasises the greater activation energy of a chemical process, as compared with a physical process.

The enthalpy change ΔH of the lattice transition is calculated with reference to pure indium (28.4 J g^{-1}) measured at 703 K. The calculated values reflect a slightly higher (21.4 J g^{-1}) value for the NH_4-form than for the Na-form (20.9 J g^{-1}). This small enthalpy rise of 0.5 J g^{-1} matches the structural shift towards higher association because of hydrogen bonding.

This preliminary discussion reveals the mutually opposing effects of enhanced cation mobility and lattice association, which control the thermodynamics of the transition. This is emphasised below in the discussion of the effect of γ-irradiation on the thermodynamics of the NH_4-form.

The contrasting effects of γ-irradiation

It is important to stress that NaX is insensitive to γ-irradiation. In contrast, NH_4X shows significant shifts when irradiated with γ-rays. The major effect of the irradiation is a consistent reduction in the C_p band width of both the NH_4^+ decomposition (Fig. 3) and the lattice transition (Fig. 4), which conforms with a reduced lattice association. In effect, the T_c of the lattice transition of the NH_4-form reverts to the lower value of the less associated Na-form (Fig. 1) upon exposion to a 10 Mrad dose. It appears that the irradiation enhances the NH_4 cation mobility which, in turns, helps in diminishing the lattice association. Consistent with this effect, the C_p

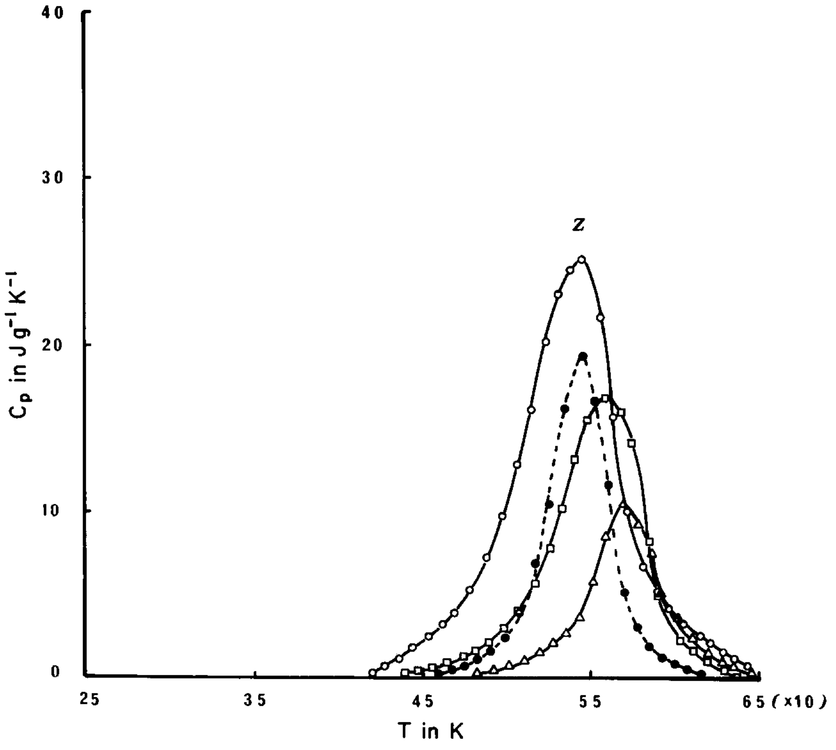

Fig. 3. Effect of γ-irradiation on the $C_p(T)$ dependence of NH_4^+ decomposition (Z) at: ○, zero; □, 5; △, 10; and ●, 20 Mrad doses.

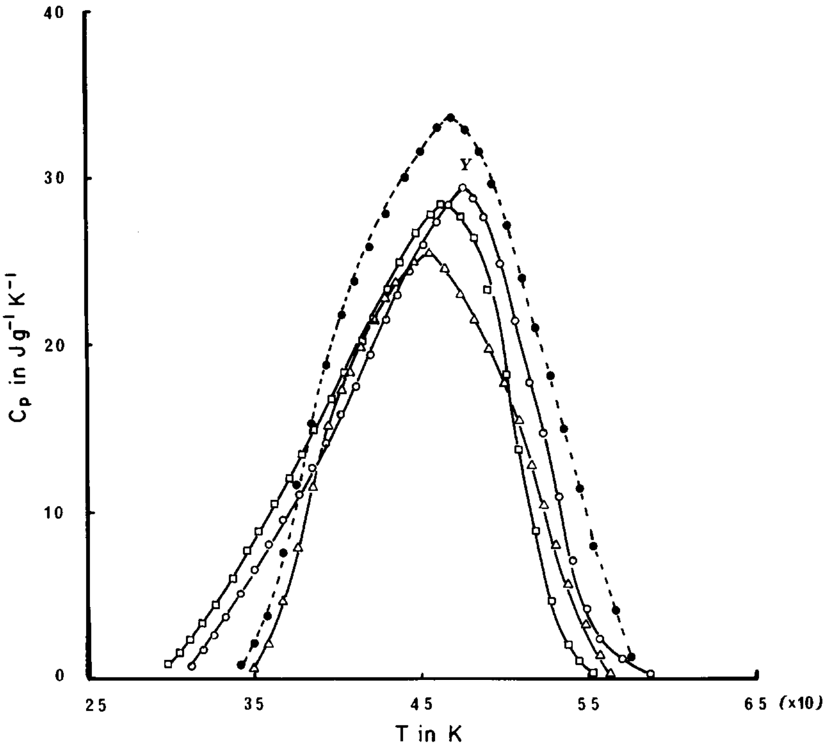

Fig. 4. Effect of γ-irradiation on $C_p(T)$ dependence of the zeolite lattice transition (Y) at: ○, zero; □, 5; △, 10; and ●, 20 Mrad doses.

values of both transitions is reduced (Figs. 3, 4), particularly at T_c, showing minimum at 10 Mrad.

The contrasting effects of enhanced cation mobility and lattice association are clearly resolved in the opposing shifts of T_c upwards (Fig. 3) for the NH_4^+ decomposition and downwards (Fig. 4) for the lattice transition, before reverting to normal above 10 Mrad.

The small NH_4^+ ions have no difficulty in diffusing and exchanging with Na^+ ions of the sodalite cage, as occurs successfully with the more accessible supercage of faujacite-type zeolite. γ-Irradiation is known to induce trapping [11, 12] as well as mobility effects. It appears that a significant number of NH_4^+ cations are trapped, probably at the less accessible sodalite cage, which is apparent in the higher C_p values above T_c (Fig. 3) for both the 5 and 10 Mrad samples. The trapped cations are apparently responsible for the higher T_c values of these particular samples. Irradiation at higher doses seems to release the trapped cations so that the T_c and C_p of the NH_4^+ decomposition revert to higher, but never their original, values. It is important to note that the NH_4^+ decomposition band diminishes progressively at higher doses, and is eventually destroyed at

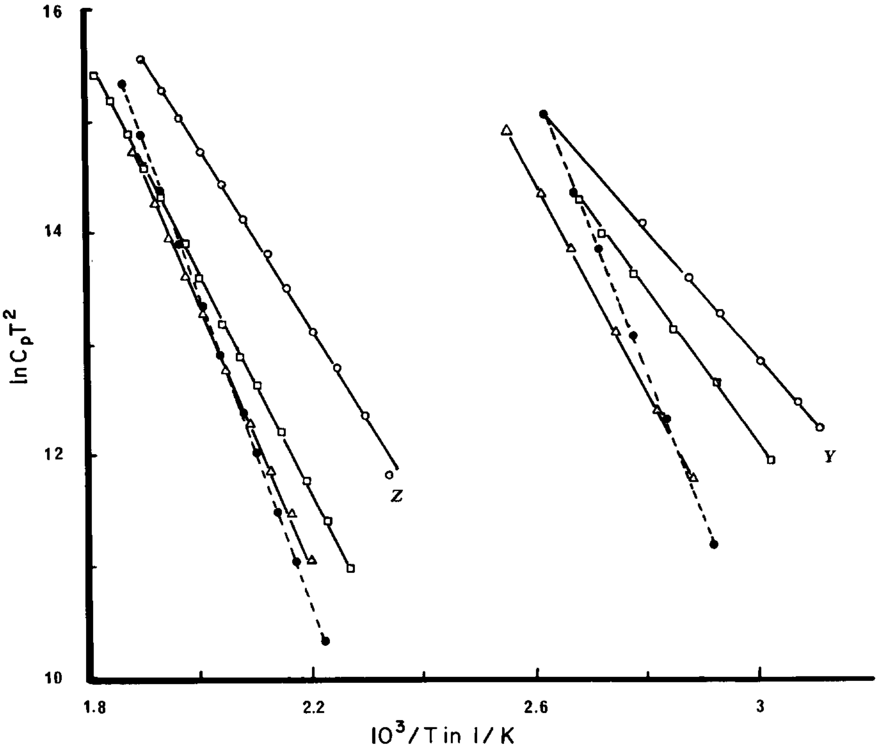

Fig. 5. Effect of γ-irradiation on the Arrhenius-like dependence of C_p on T for the NH_4^+ decomposition (Z) and the zeolite lattice transition (Y) at: ○, zero; □, 5; △, 10; and ●, 20 Mrad doses.

100 Mrad. A similar effect of γ-induced decomposition has been reported [13] for the TPA cations in ZSM-5 zeolite.

The activation energy $E^{\#}$ increases progressively with the irradation for both the NH_4^+ decomposition (Fig. 5, curve Z) and the lattice transition (Fig. 5, curve Y). In contrast with the linear dependence (Fig. 6, curve Y) of the energy of the lattice transition on the irradiation dose, the dependence of the NH_4^+ decomposition deviates, after ideal linearity (Fig. 6, curve Z) beyond 10 Mrad, towards lower activation energies. The energy loss at higher doses could be associated with a decrease in cation concentration, probably because of the severe dose-induced decomposition. Excluding the role of the high-dose cation decomposition, γ-irradiation induces a linear rise in both the cation and lattice transition activation energies. This seems to contradict with the enhanced mobility. This effect, however, can be attributed to the concurrently operating opposing effects of cation trapping and lattice defects.

Finally, it can be concluded that the possible contribution of trapped cations induces lattice defects. These govern the thermodynamics of both the cations and lattice transitions in a mutually opposing way, with respect

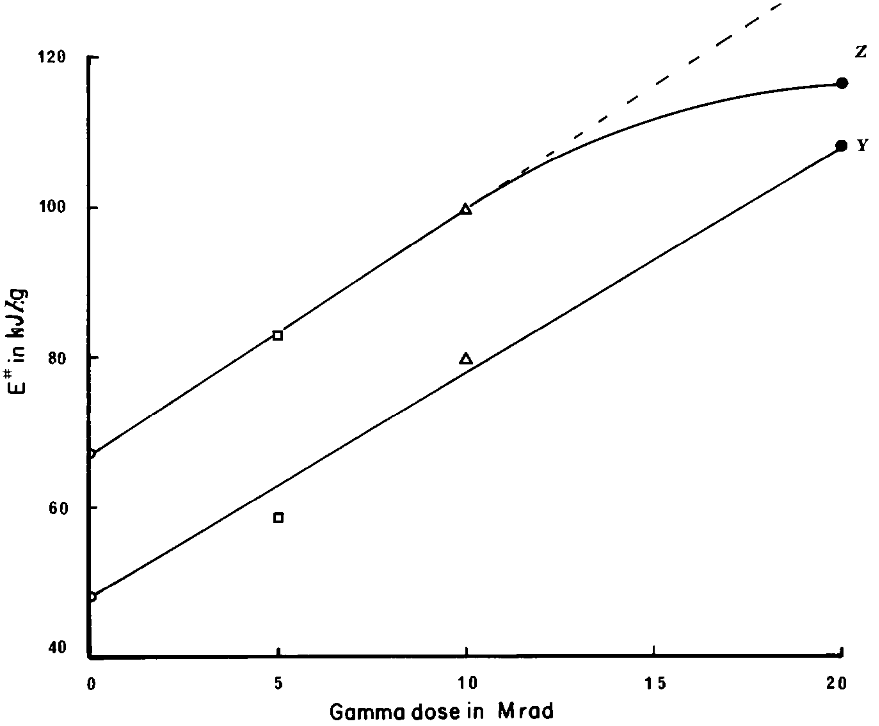

Fig. 6. Effect of γ-irradiation on the activation energy of the NH_4^+ decomposition (Z) and the zeolite lattice transition (Y).

to the enhanced mobility, which are all induced by γ-irradiation. These contrasting effects may be the origin of the hysteresis effect observed for γ-irradiation in both the previous [1] and the present studies.

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