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A thermal study of the water-assisted phase transition in ZSM-5

Part 1. Effect of aluminium loss as removal or replacement with boron and of γ irradiation on the lattice structure of HZSM-5

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Abstract

The DTA results for HZSM-5, differently modified by increased incorporation of boron in the zeolite lattice, zeolite dealumination and γ irradiation indicated the dependence of the specific heat of the endothermic peak at 363 K on the extent of the modification. The linear dependence of the change in enthalpy, entropy and activation energy on the modifier content in the case of boron, reveals the association of this peak with a structural shift induced by the boron incorporation. A similar structural shift would explain the similar dependence of these thermodynamic parameters on both the zeolite dealumination and the γ irradiation. This structure shift is attributed to a change in the lattice parameters. The critical exponent of about 0.1 confirms this assignment, as this fits the 3-d Ising model of a tetrahedral structure for the zeolite lattice. Because this endothermic peak is in the temperature range of hydration–dehydration, it is more appropriately assigned to a water-assisted phase transition, where the zeolite exchanges orthorhombic and monoclinic crystal symmetries.

INTRODUCTION

Zeolite, whether naturally occurring or synthesized, is a crystalline aluminosilicate belonging to the tectosilicate family, well known for both its widely varying Si/Al ratio and its channel structure. Varying the channel structure induces a molecular sieving feature, whereas varying the Si/Al ratio mostly affects the zeolite acidity by changing the aluminium-site population. Increasing this ratio also enhances the thermal stability of the zeolite. This is apparent from the low thermal stability of aluminium-rich zeolites, such as synthetic X- and Y-types, from the improved thermal stability of mordenite characterised by increased Si/Al ratios, and from the high thermal stabilities of highly siliceous zeolites, such as those of the ZSM family [1–5]. The improved thermal stability could be attributed to the increased replacement of silicon for aluminium [6], which results in reduced

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cell parameters as a result of the reduced bond length, from 0.175 nm for Al–O to 0.161 nm for Si–O. Indeed, the siliceous protectosilicates are the most thermally stable among these minerals. More recently, dealumination has been used to improve the thermal stability of aluminium-rich zeolites, such as the Y types [7,8].

By way of improving the shape selectivity of ZSM-5, boron has been used for replacing aluminium in the zeolite lattice; this reduces the cell parameters even more than for a pure silicalite [9]. Replacing boron or silicon for the aluminium of the zeolite should be a thermodynamically favoured process [10] that would lead to a more thermally stable material. Several investigations have focused on modified shape-selectivity, catalytic activity, acidity and structure, as induced by the boron modifier [11–14]. However, although important, the thermal properties of these modified materials have attracted less interest. A thermal study of the zeolite NaA has revealed a phase transition at 335 K, attributed to dehydration-induced structure distortion [15–17], where the zeolite exchanges rhombic and cubic crystal symmetries. ZSM-5 has been known to exhibit orthorhombic and monoclinic crystal symmetries [18,19]. The results of the thermal analysis of TPA-occluded ZSM-5 have shown a peak at 383 K, similar to the peak attributed to a phase transition in crystalline TPABr [20].

In the present study, an endothermic peak appears in the vicinity of 363 K to distinguish the H form from the Na form of ZSM-5; the latter is dominated by a much stronger exothermic peak at 723 K. The aim of this work was to investigate the endothermic peak at 363 K to characterise its sensitivity to structure shifts effected by zeolite modification by the methods discussed for the H-form zeolite.

EXPERIMENTAL

Materials

Four ZSM-5 samples were synthesised with the intention of incorporating boron at the expense of aluminium so that the resultant modified zeolite would exhibit an increased B/Al ratio, with $B + Al$ being almost unaltered [14]. The acidic form, HZSM-5, was obtained from the previously calcined parent zeolite by acid ion exchange. Synthesis of a pure boralite was also attempted [21]. However, this sample still exhibited a small aluminium content as a result of the alkali attack on the glass walls of the container during synthesis. A further zeolite sample was acid dealuminated [13]. The results of elemental analyses are shown in Table 1, as site per unit cell.

METHODS AND EQUIPMENT

The differential thermal analysis, DTA, was performed on samples weighing about 30–40 mg in the temperature range 288–1273 K at a heating rate

TABLE 1

Elemental analysis (atoms per unit cell)

Zeolite	Si	Al	B	B/Al	B+Al
$HZSM_1$-5	91.13	4.00	0.87	0.22	4.87
$HZSM_2$-5	91.90	2.80	1.30	0.47	4.10
$HZSM_3$-5	91.24	3.21	1.55	0.48	4.76
$HZSM_4$-5	91.71	2.63	1.66	0.63	4.29
H-boralite	94.47	0.28	1.25	4.46	1.53
Deal. HZSM-5	92.26	3.74	–	–	–

of 10 K min^{-1}, using a Shimadzu DSCTA 30 thermal analyser. A similar measurement was performed on these samples after their exposure to γ irradiation in air at 298 K at a dose rate of 1.45 MRad h^{-1}, the total dose being 10 MRad. A ^{60}Co γ-cell 220, manufactured by Atomic Energy of Canada Ltd., was the source of irradiation. From the thermal data, the specific heat C_p, enthalpy change ΔH, entropy change ΔS, activation energy U and critical exponent α were calculated, as reported elsewhere [22].

RESULTS AND DISCUSSION

The DTA results for previously calcined samples show a typical thermogram dominated by two endothermic peaks, one at 363 K and a much wider one centred at 1000 K. At first, the peak at 363 K might be considered to represent the dehydration transition of the zeolite. This is certainly true for the dehydroxylation peak in the vicinity of 1000 K, as previously reported for this zeolite [23] and for mordenite [24]. However, the peak at 363 K is quite sensitive to structure shifts and could be usefully employed for probing quantitatively the extent of structure modification, as will be demonstrated in this study. It has only limited association with water, as it persists for highly dehydroxylated zeolites.

The specific heat was calculated in the vicinity of 363 K. The temperature dependence of C_p (Fig. 1) shows that the heat variation extends over a wide temperature range, with no abrupt changes. The wide shape of this peak could be attributed to several factors including surface heterogeneity, bulk strain and, to some extent, a dehydration process. This three-dimensional figure also reveals the dependence of C_p on the content of the boron modifier; the analysis of this relationship may lead to further interesting thermodynamics–structure dependences. The enthalpy change, ΔH, associated with the C_p change at this peak has been determined with reference to that of standard indium. The calculated figures are reported in Table 2 and are plotted vs. boron content in Fig. 2 to show how dependent the enthalpy change is on the extent of the modification. The interesting linear depen-

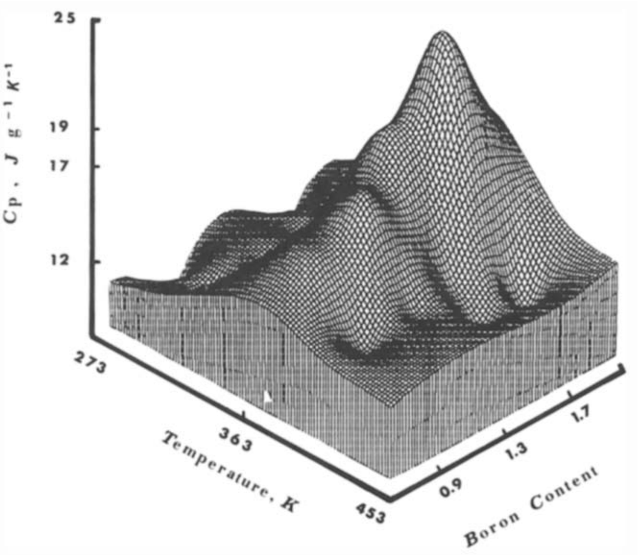

Fig. 1. A three-dimensional representation of C_p–temperature–boron content. The back peak is for $HZSM_4$-5 after γ irradiation.

dence can be expressed as a useful empirical equation for estimating the enthalpy change at any given boron content:

$$\Delta H = 0.76 \pm 0.01 + 0.83 \pm 0.01\ B$$

where B is the boron content in sites per unit cell.

Being boron dependent, the increased change in enthalpy should indicate the association of the modified thermal properties with a structure shift attributed to boron incorporation in the zeolite lattice structure. Replacing boron for aluminium reduces the lattice cell parameters, and therefore leads to a more dense zeolite phase [9]. This is consistent with the effect of zeolite dealumination [6–8,12], where silicon replaces aluminium in the lattice structure. An aluminium decrease of 28% modifies ΔH (Table 2) to an extent similar to that in the sample most modified with boron, $HZSM_4$-5.

TABLE 2

The dependence of ΔH, ΔS, U and α on the zeolite boron content

Zeolite	B	ΔH (J g^{-1})	ΔS (J g^{-1} K^{-1})	U (J g^{-1})	α
$HZSM_1$-5	0.87	1.487	0.0042	27.503	0.08
$HZSM_2$-5	1.30	1.824	0.0052	31.261	0.08
$HZSM_3$-5	1.55	2.056	0.0057	33.838	0.08
$HZSM_4$-5	1.66	2.196	0.0059	34.129	0.08
H-boralite	1.25	1.813	0.0051	27.353	0.08
Deal. HZSM-5	–	2.167	0.0060	34.669	0.08

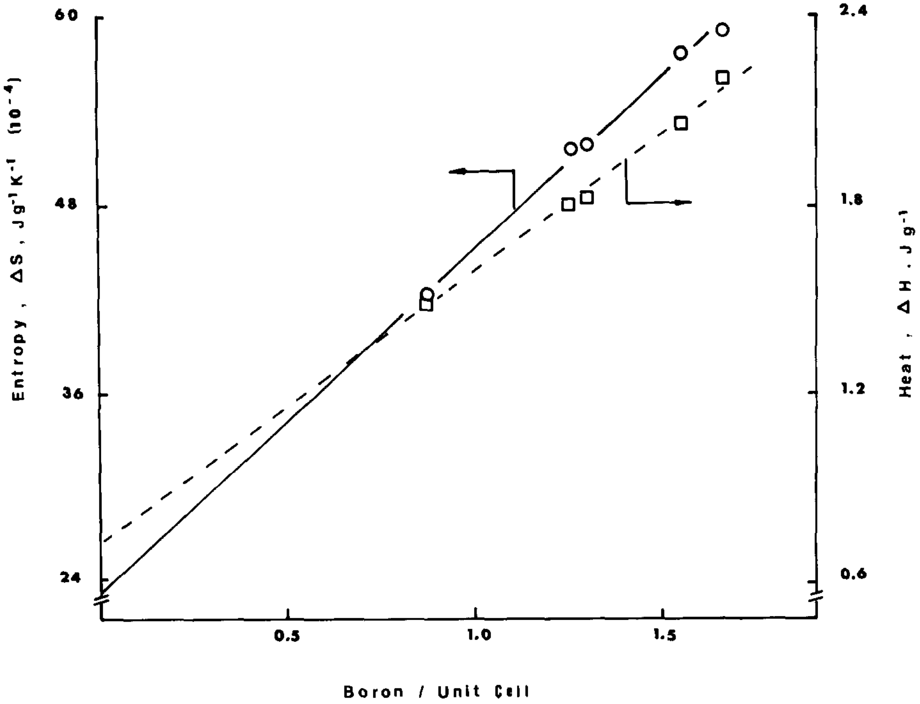

Fig. 2. The dependence of enthalpy change (right) and entropy change (left) on the zeolite boron content.

This structure dependence of the endothermic peak at 363 K suggests its assignment to a structural phase transition across the orthorhombic–monoclinic crystal symmetries [18,19]. In agreement with previous reports [15–17] and due to the fact that this phase transition takes place in the temperature vicinity of zeolite dehydration, one could assign this endothermic peak more appropriately to a water-assisted phase transition.

In addition to these different methods of lattice modification, irradiating the zeolite with γ radiation is expected to induce similar structure displacements, particularly of the lighter elements [25]. This is depicted qualitatively in Fig. 1 as a further gain in the C_p for $HZSM_4$-5, and quantitatively as a 6.52%, 11.34% and 11.74% gain in ΔH for $HZSM_1$-5, $HZSM_3$-5 and $HZSM_4$-5 respectively, i.e. the effect of γ irradiation is most pronounced at the site occupied by boron, the lightest element in the tectosilicate structure of the modified zeolite.

Removing aluminium from the lattice or replacing it by boron should introduce a lattice disorder, which could be determined thermally as an entropy change, ΔS, the thermal disorder parameter. Calculation of the entropy at the phase transition shows a linear dependence (Fig. 2) on the content of the boron modifier, which could also be true for dealumination and γ irradiation. The calculated figures are reported in Table 2, where a

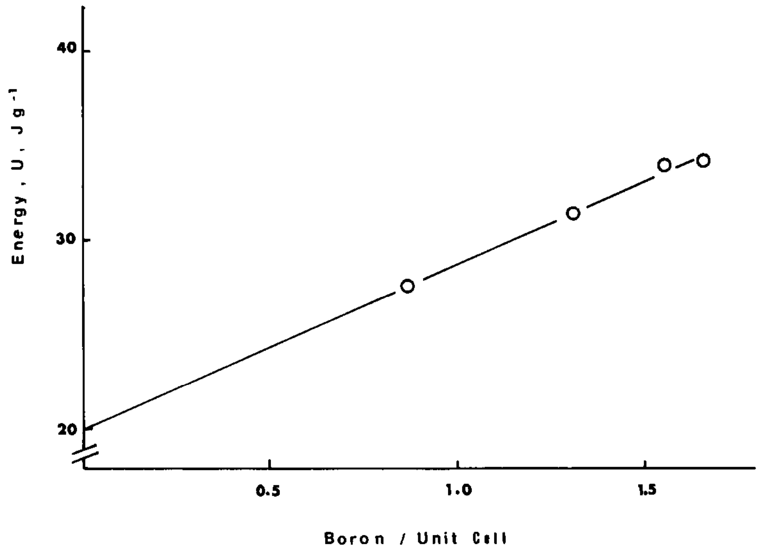

Fig. 3. The dependence of activation energy on the zeolite boron content.

similar empirical formula could be postulated for calculating the lattice disorder at any given extent of modification.

The activation energy, U, of the stimulated phase transition could be estimated by applying the exponential relation [26]

$$\Delta C_p = \left(ZNU^2/RT^2\right) e^{-U/RT}$$

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

Plotting ln $\Delta C_p T^2$ vs. $1/T$ should yield a linear relation (Fig. 3), the slope of which facilitates determination of the activation energy. This linear dependence is true experimentally away from the critical temperature. The activation energy is linearly dependent (Fig. 3) on the content of the boron modifier; the calculated values are reported in Table 2. The $U/\Delta H$ ratio ranges from 15 to 19, being lower for the sample incorporating more boron. These consistent data are not surprising, as the thermal properties of a material should be enhanced by shifting to a more dense phase. The present methods of lattice modification effect such a shift, as has been discussed in terms of the reduced cell parameters of the modified zeolite.

Finally, it is of great interest to investigate the model to which this phase transition might be referred. The excess heat capacity, ΔC_p, reveals a useful physical parameter [27] when correlated with the term t:

$$\Delta C_p = At^{-\alpha}$$

where A is a constant, $t = (T - T_c)/T_c$ and α is the parameter indicative of the phase transition model. This parameter can be determined directly from

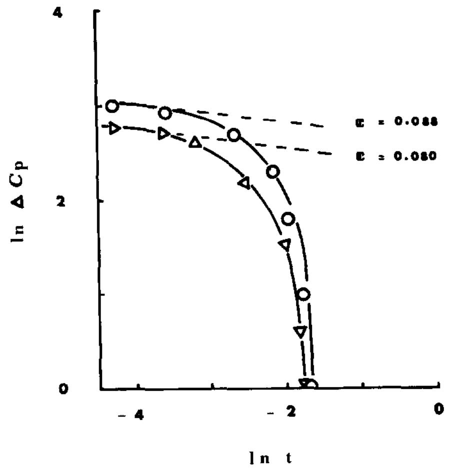

Fig. 4. Effect of γ irradiation on the critical exponent of $HZSM_4$-5. The upper curve is for the irradiated sample; a minor shift of 0.008 to higher values is observed.

the slope of ln ΔC_p vs. ln t near the critical temperature. The resultant critical exponent is found to be similar for all the samples (Table 2) and to approach the value of 0.1, characteristic of the 3-d Ising model [28,29], which illustrates the tetrahedral network structure of the zeolite lattice. This is clear evidence that the endothermic peak at 363 K of HZSM-5 is associated strongly with the zeolite structure. Although γ irradiation enhances the thermodynamics of the zeolite, it has no destructive effect on the zeolite structure, as the critical exponent of the 3-d Ising model (Fig. 4) is retained.

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REFERENCES

1 D.W. Breck, Zeolite Molecular Sieves, Wiley, New York, 1974.
2 J.V. Smith, in J.A. Rabo (Ed.), Zeolite Chemistry and Catalysis, ACS Monogr., 171 (1976) 1.
3 W.M. Meier and D.H. Olson, Atlas of Zeolite Structure, Juris Druck and Verlag, Zurich, 1978.
4 L.B. Sand, in L.V.C. Rees (Ed.), Proc. 5th Int. Conf. on Zeolites, Heyden, London, 1980, p. 1.
5 W.J. Mortier, Compilation of Extra Framework Sites in Zeolites, Butterworth Science, London, 1982.
6 G.T. Kerr, A.W. Chester and D.H. Olson, Acta Phys. Chim., 24 (1978) 169.

7 C.V. McDaniel and P.K. Maher, in J.A. Rabo (Ed.), Zeolite Chemistry and Catalysis, ACS Monogr., 171 (1976) 285.

8 H.K. Beyer and I. Belenykaya, in B. Imelik, C. Naccache, Y. Ben Taarit, J.C. Vedrine, G. Coudurier and H. Praliaud (Eds.), Catalysis by Zeolites, Elsevier, Amsterdam, 1980, p. 203.

9 M. Taramasso, G. Peregro and B. Notari, in L.V.C. Rees (Ed.), Proc. 5th Int. Conf. on Zeolites, Heyden, London, 1980, p. 40.

10 S. Beran, P. Jiro and B. Wichterlova, React. Kinet. Catal. Lett., 18 (1981) 51.

11 M.B. Sayed and J.C. Vedrine, J. Catal., 101 (1986) 43.

12 M.B. Sayed, J. Chem. Soc. Faraday Trans. 1, 83 (1987) 1751.

13 M.B. Sayed, Thermochim. Acta, 126 (1988) 325.

14 M.B. Sayed, A. Auroux and J.C. Vedrine, J. Catal., 116 (1989) 1.

15 T. Rayment and J.M. Thomas, Zeolites, 3 (1983) 2.

16 J.M. Bennett, C.S. Blackwell and D.E. Cox, ACS Symp. Ser. 218, American Chemical Society, Washington, DC, 1983, p. 143.

17 C.B. Belbeach, W. Roulliay, R. Khan and E. Cohen de Lara, Zeolites, 3 (1983) 99.

18 G.T. Kokotailo, S.L. Lawton, D.H. Olson and W.M. Meier, Nature 437.

19 D.H. Olson, G.T. Kokotailo, L.S. Lawton and W.M. Meier, J. Phys. Chem., 85 (1981) 8238.

20 A. Nastro, P. Ciambelli, F. Crea and R. Aiello, J. Therm. Anal., 33 (1988) 941.

21 G. Coudurier and J.C. Vedrine, Pure Appl. Chem., 58 (1986) 1389.

22 T. Daniel, Thermal Analysis, Kegam Page, London, 1973, p. 127.

23 H. Siegel and H. Splinder, J. Therm. Anal., 33 (1988) 903.

24 B. Hunger, J. Hoffmann and P. Mothsche, J. Therm. Anal., 32 (1987) 2009.

25 R. Ravi and P.S. Narayannan, Ferroelectrics, 139 (1981) 1221.

26 V.P. Burtseva, V.E. Vasilev and V.M. Varikash, Sov. Phys.-Solid State, 30(5) (1988) 877.

27 L.P. Kadanoff, W. Gotze, D. Hamblen, R. Hetch, E.A.S. Lewis, V.V. Palciauskas, M. Rayl, J. Swift, D. Aspnes and J. Kane, Rev. Modern Phys., 29(2) (1967) 395.

28 M.F. Sykes, J.L. Martin and D.L. Hunter, Proc. Phys. Soc., 91 (1967) 671.

29 D.S. Gaunt and C. Domb, J. Phys. C (Proc. Phys. Soc.) Ser. 2(I), (1968) 1038.