

PHYSICO-CHEMICAL CHARACTERIZATION OF FERRIC EXCHANGED Y ZEOLITES *

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ABSTRACT

Ferric exchanged Y zeolites are prepared by ion exchange and are characterized by X-ray diffraction, thermal analysis, IR and visible spectroscopy. The number of hexa-aquo complexes, $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$, in supercages is determined from thermal analysis, and cation distribution at different sites is discussed. The visible spectra confirmed the formation of hexa-aquo complexes of iron in freshly prepared hydrated FeNaY zeolites. The migration of ferric ions from the supercage to the sodalite cage or hexagonal prism takes place on activation of Fe^{3+}Y zeolites at 500°C for 2–10 h. The thermal stability of the activated samples is discussed on the basis of X-ray and thermal analysis.

INTRODUCTION

Synthetic zeolites exchanged with ferric ions are expected to be good acidic catalysts. However, the loss of crystallinity and thermal stability is reported for these catalysts. The difficulties in preparing ferric exchanged zeolites without structure breakdown have been discussed [1,2]. Malashevich and co-workers [3] found that zeolites with low silica content, types A and X, retain their crystalline structure up to 15–17% substitution of sodium by ferric ions. Morice and Rees [4] reported that exchange without decomposition could be obtained by contacting Y zeolite to $\text{Fe}(\text{NO}_3)_3$ solution for a short time. Delgass et al. [5] prepared ferrous exchanged zeolites under an atmosphere of nitrogen and obtained the ferric forms by oxidation. Badran et al. [6] obtained ferric ion exchanged A and X zeolites using an ethereal solution of $\text{Fe}(\text{SCN})_3$ and buffer solutions. The loss of crystallinity appears to be dependent on both temperature and pH of the solution used for ion exchange.

Attempts have been made to understand the structural aspects of iron exchanged Y zeolites, particularly by Mössbauer spectroscopy [5,7–9].

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Boudart and co-workers [7,8] established the redox behaviour of iron in Y zeolites by Mössbauer and IR spectroscopy, and proposed the presence of $\text{Fe}^{3+} - \text{O}^{2-} - \text{Fe}^{3+}$ inside the sodalite cages after thermal treatment. Nesterov et al. [10] observed that ESR spectra of a fresh FeNaY sample did not differ from those of hydrated NaY while dehydrated samples showed a line with $g = 4.31$, the intensity of which increased with the dehydration temperature up to 450°C . They concluded that after cation exchange, ferric ions are located in supercages in hexa-aquo form with octahedral symmetry; but with increasing dehydration temperature ($> 500^\circ\text{C}$), ferric ions penetrate into the smaller cavities.

It was thought of interest to investigate the nature of the aquo complex of iron in zeolite, the exact temperature at which the dehydroxylation of possible $[\text{Fe}(\text{OH})_6]^{+(3-)}]$ species takes place, the cation site distribution in hydrated and dehydrated forms, migration of ferric ions, and the thermal stability of ferric exchanged Y zeolites with respect to different per cent ferric exchanges.

EXPERIMENTAL

Catalyst preparation

Linde NaY zeolite, binder free (SK-40), obtained from Union Carbide, U.S.A., was used as starting material for catalyst preparation. The ferric exchanged zeolites were prepared by treating NaY with aqueous solutions of ferric acetate-acetic acid at about pH 4 at $27-30^\circ\text{C}$ with constant stirring. After cation exchange, the zeolite was filtered, washed with distilled water several times till free of acetate ions, and oven-dried at 120°C for about 20 h, cooled, powdered and kept over saturated ammonium chloride solution in a desiccator.

Up to 75% exchange, the samples were prepared in a single ion exchange process indicating that the exchange of sodium ions present in supercages by ferric ions is a thermodynamically favourable process, which is due to the fact that the hydration energy of ferric ion is higher than that of sodium ion. However, it was difficult to exchange sodium in the zeolite above 82%, because bulky hydrated ferric ions do not enter into the hexagonal prisms to replace sodium ions present at site I. A successful attempt was also made to prepare ferric exchanged Y zeolites in non-aqueous solutions. Ferric exchanged Y zeolites were prepared by treating NaY with the ferric chloride-ethanolic solution. The X-ray diffraction patterns showed that the zeolite samples prepared in non-aqueous media were highly crystalline.

The X-ray diffraction patterns of hydrated zeolite powder samples were recorded on a Philips X-ray diffractometer Model PW 1060/00, using $\text{Cu } K_\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$).

All thermograms were recorded under identical conditions on an automatic Hungarian derivatograph (Model-MOM-102). The sample weight was 300 mg and the heating rate was $6^{\circ}\text{C min}^{-1}$. The pre-heated γ -alumina was used as a reference material.

The IR spectra were recorded in the frequency range $250\text{--}1300\text{ cm}^{-1}$ using a Perkin-Elmer 221 spectrometer. The nujol mull or KBr pellets of the hydrated samples were used for recording the spectra.

The visible spectra were recorded at room temperature in the range $200\text{--}800\text{ nm}$ on a specord UV-vis, Carl-Zeiss spectrometer using KBr pellets of the hydrated samples.

Thermal stability

To investigate the effect of thermal treatment, NaY, FeNaY(37) and FeNaY(82) zeolites were heated at 500°C for 2 and 10 h. The final temperature, 500°C , was achieved at a heating rate of $5^{\circ}\text{C min}^{-1}$. After thermal treatment, the samples were cooled and kept over saturated ammonium chloride solution in a desiccator for 1 week for water saturation.

RESULTS

X-Ray diffraction

The intensities and 2θ values for NaY zeolite are in agreement with the published data. All the samples were crystalline with Fd3m crystallographic group and without significant change in lattice parameters. However, with respect to the increase in per cent ferric exchange, there was a decrease in relative intensities of 311, 331 and 511, 440, 532, 542, 751 and 551 *hkl* planes, which could be due to the smaller total number of counter-cations in the exchanged form (three sodium ions are replaced by one ferric and the ionic radius of ferric is smaller than that of sodium). Considering the 533 plane which is least affected by ion exchange with reference to NaY, at higher ferric exchanges ($> 60\%$) the distortion of framework due to ferric ions may be a possible explanation for the decrease in intensities.

IR spectra

The IR spectra of FeNaY zeolites have the general features [11] of the original NaY zeolite with some additional details of the characteristic bands showing the specific influence of the polyvalent counter-cation. With the increase of ferric exchange the IR bands are broadened due to a strong ferric-framework interaction. The spectra did not indicate structural breakdown on ferric exchange. In the case of NaY, FeNaY(44), FeNaY(75) and

FeNaY(82), the double ring bands were observed at 561.80, 561.80, 558.66 and 555.56 cm^{-1} , respectively. At a higher degree of ferric exchange, ferric ions occupy sites I or I', thereby strongly interacting with the double ring. The IR data thus confirmed that the basic Y zeolite structure was preserved during ferric exchange.

Visible spectra

Ferric exchanged Y zeolites are yellowish in colour. With increase in iron content, the colour changes from yellow to yellowish-brown. The ferric ion in aqueous solution is very much subject to hydrolysis and the yellow colour is not due to ligand field bands of $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, but rather charge transfer. The nature of hydration of ferric ions in aqueous solution is established by magnetic susceptibility and spectral methods [12,13]. The FeNaY samples exhibit a broad band at about 350 nm. The absorbance increases linearly with the increase of iron content in the zeolite samples as shown in Fig. 1. It should be noted that $\epsilon\text{-Fe}(\text{OH})^{2+}$ reaches about 5000 (maximum) near 350 nm [12] while the $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ band lies at about 240 nm. We conclude that every ferric ion in hydrated Y zeolite has a hydroxyl group attached to it (up to 82% exchange).

Thermal analysis

Figure 2 shows typical thermograms for NaY and FeNaY zeolites. Table 1 shows the peak temperatures for all the samples investigated.

The NaY zeolite shows a single endothermic peak due to dehydration at 80–320°C. The exothermic peak corresponding to the structure breakdown

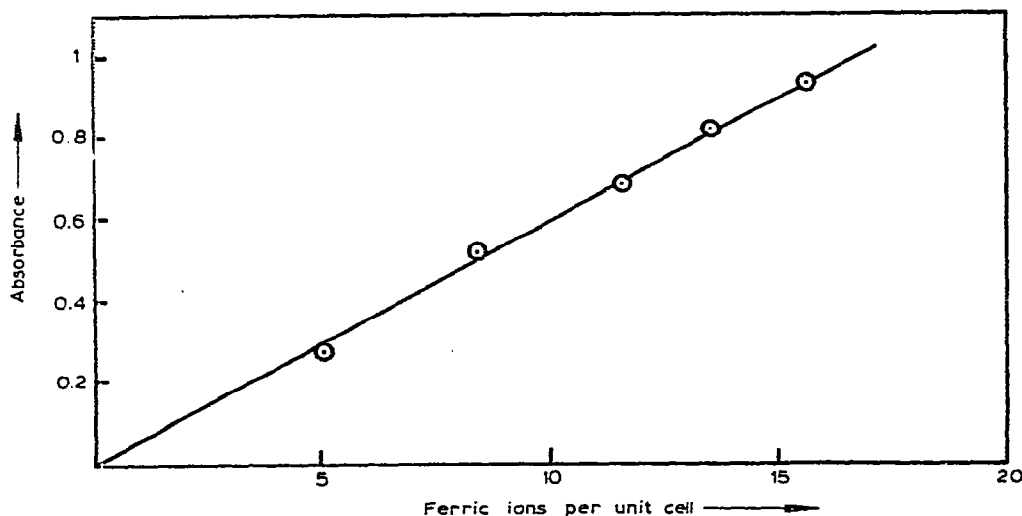


Fig. 1. A plot of absorbance at 350 nm vs. ferric ions per unit cell.

of the zeolite is at 842°C. On the other hand, the DTA curves for the iron exchanged zeolites exhibit three endothermic peaks between 160 and 400°C and one exothermic peak at 840–870°C.

FeNaY(37), FeNaY(44), FeNaY(61) and FeNaY(75) (where the figures in parentheses indicates % Fe³⁺ exchange), show the first endothermic peak maxima at 165, 170, 160 and 160°C, respectively, corresponding to the desorption of physically adsorbed and weakly chemisorbed water on to the framework oxygens through O---H linkages. In the case of higher exchanged FeNaY(82), this peak shows further splitting with minima at 110 and 160°C. A second endothermic peak occurs at 290°C which is due to desorption of

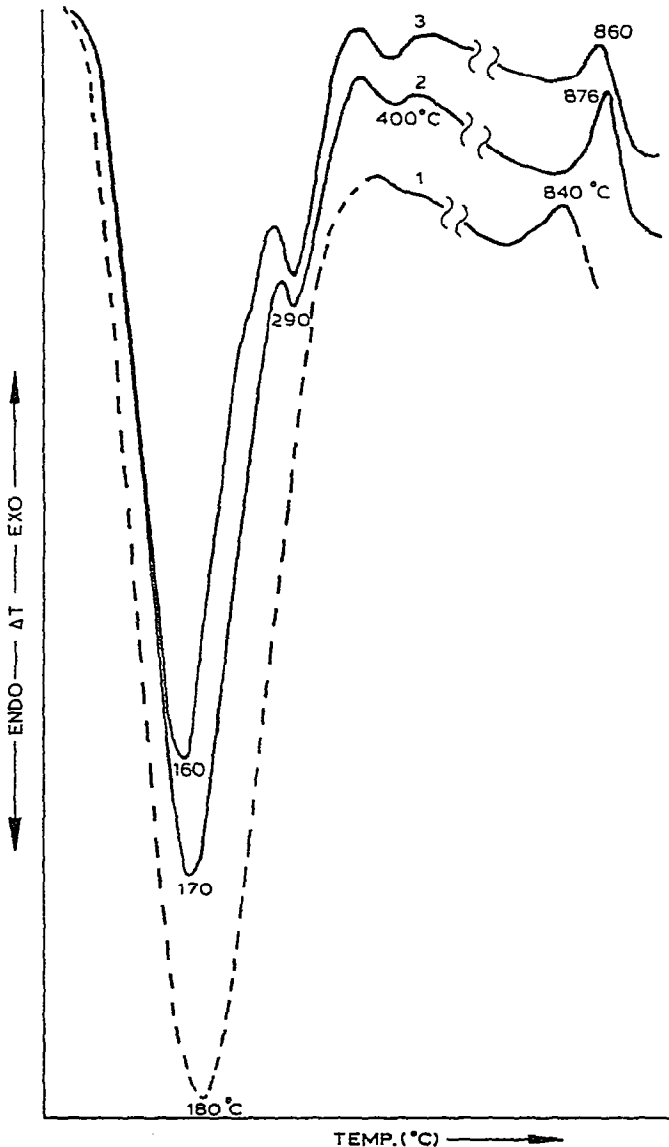


Fig. 2. DTA curves of (1) NaY (— — —), (2) FeNaY(44), and (3) FeNaY(61).

TABLE I
Composition of zeolites and peak temperatures in DTA

Zeolite ^a	Unit cell composition	Endothermic peak (°C)				Exo-thermic peak (°C)
		First peak	Second peak	Third peak	Endo-thermic peak end	
NaY	Na ₅₇ (AlO ₂) ₅₇ (SiO ₂) ₁₃₅ (268 H ₂ O)	180			360	840
FeNaY(37)	Fe ₅ Na ₃₉ H ₃ (AlO ₂) ₅₇ (SiO ₂) ₁₃₅ (269 H ₂ O)	165	290	395	430	870
FeNaY(44)	Fe _{8.4} Na _{29.6} (H ₂)(AlO ₂) ₅₇ (SiO ₂) ₁₃₅ (272 H ₂ O)	170	290	400	436	870
FeNaY(61)	Fe _{11.6} Na ₁₉ H ₃ (AlO ₂) ₅₇ (SiO ₂) ₁₃₅ (251 H ₂ O)	160	290	400	440	860
FeNaY(75)	Fe _{13.5} Na ₁₃ H ₃ (AlO ₂) ₅₇ (SiO ₂) ₁₃₅ (228 H ₂ O)	160	290	400	430	850
FeNaY(82)	Fe _{15.6} Na _{10.2} (AlO ₂) ₅₇ (SiO ₂) ₁₃₅ (252 H ₂ O)	110 and 160	295	395	440	850

^a Figures in parentheses signify percent exchange.

water coordinated to ferric ions. A third endothermic peak at 400°C is assigned to the dehydroxylation of the hydroxyl groups attached to ferric ions. The exothermic peaks for the exchanged samples are at 870, 870, 860, 850 and 850°C, respectively. All the samples show dehydroxylation of framework hydroxyl groups above 450°C.

The number of water molecules in the hydrated samples determined from chemical analysis and the TG curves are given in Table 2. The total number of water molecules per unit cell decreases with the increase in the iron content in the zeolite and is attributed to the hindrance to the sorption by the coordination complexes of Fe^{3+} ions in supercages. The number of water molecules which are physically adsorbed or weakly chemisorbed on the framework oxygens also decreases with the increase in the iron content in zeolite. The lower number of water molecules (228.0) in FeNaY(75) particularly compared to FeNaY(82) is due to framework distortion observed in crystallographic planes but cannot be correlated linearly.

The second endothermic peak at 290°C may be ascribed to the water coordinated to ferric ions. This is justified by the fact that the number of coordinated water molecules increases with the increase in the number of ferric ions in the supercages. The water molecule coordinated with Na^+ ion in NaY is in continuous exchange with the physically adsorbed water molecules, while in the case of FeNaY the coordinate bonding between water molecules and ferric ion is sufficiently strong to make them thermally distinct as compared to other molecules. This is supported by Coughlan and Carroll [14] who give the value of water solvation energy of Fe^{3+} ion as 1385 kJ mole^{-1} which is very much larger than that of Na^+ ion which is 403 kJ mole^{-1} .

The third endothermic peak at 400°C is due to the dehydroxylation of OH groups attached to ferric ions. The number of water molecules corresponding to this peak increases in a ratio of approximately 1:1 with the increase in the number of ferric ions. The dehydroxylation above 450°C is due to the removal of framework oxygens and Brønsted acid centres and may be represented as

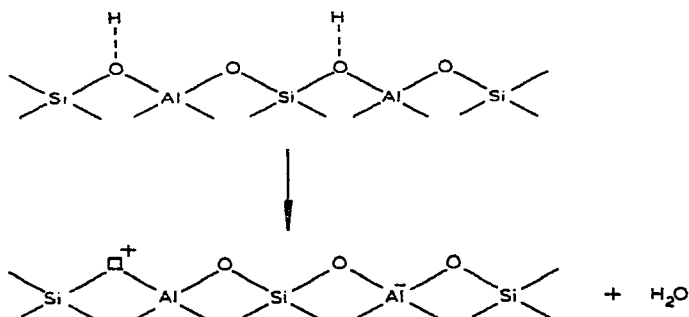


TABLE 2
Per cent weight loss and number of water molecules desorbed per unit cell

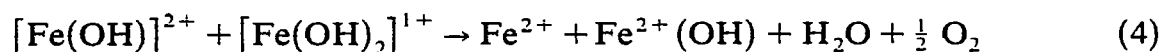
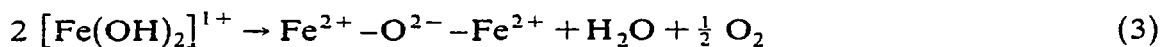
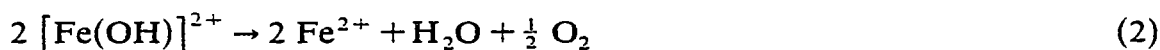
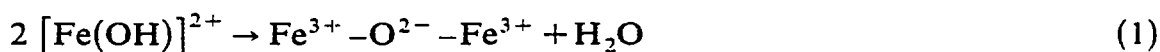
Zeolite	No. of ferric ions/unit cell	Per cent wt. loss				Above 450°C
		Total by ignition method	Total by TG method	First peak	Second peak	
NaY		27.91	27.50	26.00		1.50
FeNaY(37)	5	27.24	27.50 (268.00) ^a	23.00 (253.4)	2.50	0.50 (14.6)
FeNaY(44)	8.4	27.40	27.20 (269.5)	21.66 (225.7)	3.00 (24.5)	1.54 (14.7)
FeNaY(61)	11.6	26.40	27.20 (272.0)	19.66 (216.6)	3.48 (30.0)	1.88 (15.4)
FeNaY(75)	13.5	24.90	25.20 (251.0)	18.40 (187.3)	3.60 (33.2)	1.84 (17.9)
FeNaY(82)	15.6	26.28	26.33 (228.0)	18.66 (166.5)	4.33 (32.6)	2.00 (16.4)
			26.33 (251.5)	18.66 (178.2)	4.33 (41.4)	2.00 (19.1)

^a The values given in parentheses indicate the number of water molecules desorbed per unit cell.

DISCUSSION

Dehydroxylation

The third endotherm in DTA at 400°C is attributed to the dehydroxylation of hydroxyl groups attached to ferric ions. Mössbauer studies [7] also support the dehydroxylation process around 400°C. The absorption band at 350 nm of FeNaY confirm the presence of $[\text{Fe}(\text{OH})]^{2+}$ type species. The simultaneous analysis of DTA and TG indicates that during dehydroxylation approximately one water molecule is desorbed per ferric ion, as given in Table 2. The scheme for the dehydroxylation of $[\text{Fe}(\text{OH})]^{2+}$ may be analyzed as



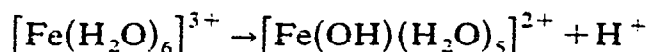
Reactions (1)–(4) have been proposed and discussed by Garten et al. [7]. Based on the TG data we propose reaction (5) for the dehydroxylation process, along with reactions (1) and (2). Reactions (3) and (4), however, do not satisfactorily explain the thermal data given in Table 2.

Aquo complex of iron

The first endothermic peak at about 170°C is characteristic of all Y zeolites. The ferric exchanged Y zeolites showed a second distinct peak at 290°C, which is attributed to water molecules coordinated to ferric ions. Morice and Rees [4] and Garten et al. [7] observed that on sorption of water there was a decrease in the quadrupole splitting in the Mössbauer spectra of FeNaY, indicating an increase in symmetry around the ferric ion. This shows that the sorbate molecules are occupying vacant coordination positions around these ions. Further, the Mössbauer studies confirm solvated ferric ions having octahedral symmetry in the hydrated state.

Aquo complexes of iron ions in water were characterized by Sillen [12], and Mulay and Selwood [13] by magnetic susceptibility and spectral methods. The binuclear ferric ion is diamagnetic as a result of exchange interaction between the adjacent ferric ions. Since FeNaY is paramagnetic, the presence of binuclear ferric ion is ruled out. Iron ion has a strong tendency to form coordination complexes with molecules or anions which can share a lone pair of electrons. The dissociation of hexa-aquo complexes of ferric ions

may be represented as



We propose the presence of $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ in supercages of hydrated FeNaY zeolite.

Cation distribution

The cations can occupy different sites in Y zeolite cages. The cations occupying sites I' and II' in sodalite cages have tetrahedral symmetry. The cations at site I in the hexagonal prism have octahedral symmetry while those at sites II or III in supercages may have tetrahedral or octahedral symmetry. The aquo complex $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ has octahedral symmetry and, considering the steric hindrance, this complex should exist in the supercages near site II. Considering the bond length of Fe-OH₂ is 2.07 Å [15] and the diameter of the supercage of Y zeolite is 11.6 Å, it is reasonable to assume that each supercage may accommodate only one hexa-aquo complex. Thus the maximum number of hexa-aquo complexes can be eight per unit cell.

In the case of hydrated FeNaY(44), about eight ferric ions are present per unit cell. Out of eight ferric ions, six should be in the supercages, which explains the liberation of 30 water molecules corresponding to the second endothermic peak, as given in Table 2. The remaining two cations occupy sites I' or II' in the sodalite cage. The $[\text{Fe}(\text{OH})]^{2+}$ species in tetrahedral coordination are present in sodalite with iron strongly interacting with three framework oxygens and the hydroxyl group extending to the centre of the sodalite. The preferential occupancy of sites I, I' or II' increases after 44% exchange. The cation distribution in the hydrated state is summarized in Table 3. During dehydration above 400°C, ferric ions from site II migrate to

TABLE 3

Cation distribution (in the hydrated state)

Zeolite	Ferric ions		Sodium ions	
	Site II*	Sites I, I' or II'	Site II	Sites I, I' or II'
NaY			32	25
FeNaY(37)	5 (25 H ₂ O)		14	25
FeNaY(44)	6 (30 H ₂ O)	2.4	11.6	18
FeNaY(61)	6.6 (33 H ₂ O)	5.0	9.0	10
FeNaY(75)	6.6 (33 H ₂ O)	6.9	9.0	4
FeNaY(82)	8.2 (41 H ₂ O)	7.4	6.2	4

site II' or a few may occupy site I in the hexagonal prism at higher exchanges. The migration of cations was discussed by Coughlan and Kilmartin [16].

Thermal stability

Table 4 shows the analysis of X-ray diffractograms of thermally treated samples. In the case of NaY and FeNaY(37), there was no significant change in unit cell parameter for the parent and thermally treated samples. The small variation in relative intensities of the diffraction lines may be associated with the dehydroxylation and cation migration. In the case of FeNaY(82), the unit cell parameter a_0 decreases as a result of thermal treatment, indicating unit cell contraction or lattice distortion. The values of unit cell parameters for FeNaY(82), FeNaY(82) (500°C, 2 h) and FeNaY(82) (500°C, 10 h) are 24.614, 24.515 and 24.456 Å, respectively.

On calcination at 500°C, the dehydration peak in NaY shifts towards a lower temperature, indicating removal of framework hydroxylated water. DTA of FeNaY(37) and FeNaY(82) shows a shift of the first endothermic peak towards lower temperatures on thermal treatment as given in Table 5.

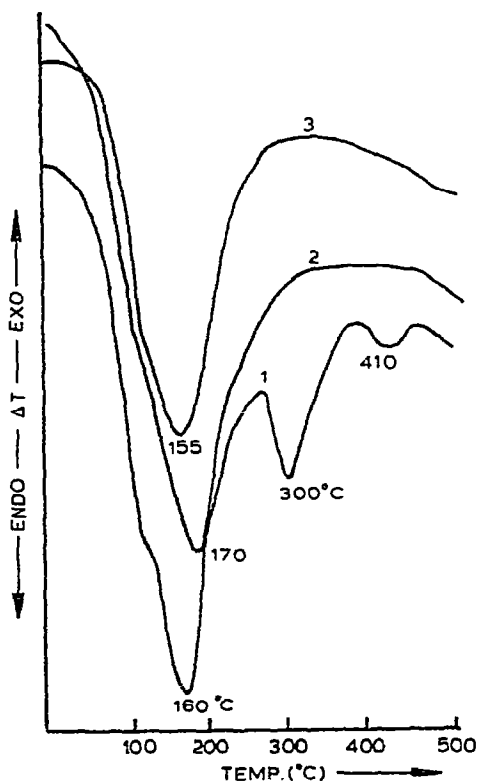


Fig. 3. Effect of thermal treatment. DTA curves of (1) FeNaY(82), (2) FeNaY(82) (500°C, 2 h), and (3) FeNaY(82) (500°C, 10 h).

TABLE 4
X-Ray intensities and unit cell constants

<i>hkl</i>	NaY	NaY (500°C, 10 h)	FeNaY(37)	FeNaY(37) (500°C, 10 h)	FeNaY(82)	FeNaY(82) (500°C, 2 h)	FeNaY(82) (500°C, 10 h)
	$a = 24.601 \text{ \AA}$	$a = 24.662 \text{ \AA}$	$a = 24.586 \text{ \AA}$	$a = 24.600 \text{ \AA}$	$a = 24.614 \text{ \AA}$	$a = 24.515 \text{ \AA}$	$a = 24.456 \text{ \AA}$
111	100.0	100.0	100.0	100.0	100.0	100.0	100.0
220	20.2	22.8	19.1	24.0	24.1	26.6	44.9
311	24.6	19.2	28.0	18.6	17.7	25.4	30.0
331	90.2	63.0	85.1	67.2	57.7	69.2	67.7
333 and 511	54.7	27.4	53.0	35.8	27.7	48.5	44.1
440	60.7	43.3	52.4	53.9	41.2	41.4	58.3
620	19.1	13.7	19.6	18.1	12.9		
533	89.1	64.8	81.6	78.9	55.9	71.6	81.9
622		6.8		8.8			
711 and 551	18.0	9.6	17.9	12.3	10.6		
642	74.7	50.2	68.5	56.4	40.0	42.0	52.0
731 and 553	20.8	9.1	17.9	16.2	11.2		
733	17.5	20.6	18.5	19.6	20.0	16.6	21.3
822 and 660	27.3	24.7	25.6	27.0	28.2	23.7	21.3
751 and 555	61.2	55.7	56.0	61.3	49.4	38.5	37.0
840	20.8	23.7	20.8	20.6	18.8		

TABLE 5
Effect of thermal treatment on DTA

Catalyst	First endotherm for dehydration (°C)	Completion of first endotherm (°C)	Exotherm for structure breakdown (°C)
NaY	180	360	840
NaY(500, 2)	165	325	870
NaY(500, 10)	165	320	850
FeNaY(37)	165	380	870
FeNaY(37, 500, 2) ^a	165	330	900
FeNaY(37, 500, 10)	155	330	900
FeNaY(82)	160	380	880
FeNaY(82, 500, 2)	170	375	875
FeNaY(82, 500, 10)	155	315	870

^a FeNaY(37, 500, 2) represents 37% ferric exchange, heated at 500°C for 2 h.

This is due to the decrease of strongly bonded water molecules in the zeolites. The trend in the change of exothermic peak temperature corresponding to the structure breakdown indicates that the thermal stability of FeNaY(37) increases while that of FeNaY(82) decreases as is also evidenced from X-ray data.

A significant change in the DTA curve for FeNaY(82) observed on thermal treatment is shown in Fig. 3 and is true in the case of all ferric

TABLE 6
Effect of thermal treatment on TG-per cent weight loss

Catalyst	TG per cent wt. loss			
	Total	Region of first endotherm	Region of second endotherm	Region of third endotherm
NaY	27.5	26.0		
NaY(500, 2)	26.0	24.25		
NaY(500, 10)	25.75	24.25		
FeNaY(37)	27.5	22.0	3.0	1.0
FeNaY(37, 500, 2)	25.25	23.5		
FeNaY(37, 500, 10)	25.25	24.0		
FeNaY(82)	26.4	19.5	4.0	1.25
FeNaY(82, 500, 2)	23.0	19.5	2.5 ^a	1.0 ^a
FeNaY(82, 500, 10)	21.5	17.5	1.7 ^a	1.0 ^a

^a No distinct DTA peak was observed.

exchanged samples. It is interesting to note that after heating at 500°C for 10 h in air and on subsequent hydration, the second and third endothermic peaks corresponding to water coordinated to iron, i.e. $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$, were absent, indicating irreversible migration of ferric ions from supercages into the sodalite cages or hexagonal prisms.

The water content in NaY decreases by about 1.5% on thermal treatment, as given in Table 6. The comparison between FeNaY(37) and FeNaY(37.500.10) shows 1.75% decrease in total water content and 2% increase in weight loss corresponding to the first endotherm. On thermal treatment, ferric ions irreversibly migrate into sodalite cages or hexagonal prisms and hexa-aquo complexes of iron do not exist. The existence of $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ complexes in supercages hinders the incoming water molecules, thereby reducing the water adsorption capacity. The decrease in TG-per cent weight loss for FeNaY(82) is due to lattice distortion, as is shown by X-ray data. Thus FeNaY(37) is thermally more stable than FeNaY(82).

CONCLUSIONS

(1) The existence of $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ in supercages of fresh, hydrated FeNaY is proposed on the basis of thermal analysis and visible spectra. (2) The dehydroxylation of the hydroxyl group attached to the ferric ion occurs at 400°C showing a distinct peak in DTA. (3) Up to 82% ferric exchange Y zeolite samples were found to be highly crystalline. The migration of ferric ions from the supercage to the sodalite cage or hexagonal prism takes place on activation of Fe^{3+} Y zeolites at 500°C for 2–10 h. (5) Thermal stability data showed that 37% ferric exchanged Y zeolite is stable after heating at 500°C, while 82% ferric exchanged sample showed lattice distortion.

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