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Studies on the Stability of Fe^{3+} Ions in the Ferrisilicate Analog of Zeolite Beta

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The influence of pretreatments such as calcination in air, evacuation, and reduction in hydrogen at different temperatures on the stability of Fe^{3+} ions in the lattice of zeolite beta are reported. The concentration of Fe^{3+} ions in the lattice has been estimated by Mössbauer spectroscopy and ion-exchange studies. XRD and catalytic test reactions have been used to further characterize the samples. Mössbauer and ion-exchange studies indicate the formation of octahedral Fe^{3+} species (defect sites) with ion-exchange capacity on calcination in air. *In situ* Mössbauer spectroscopy has been used to identify the various Fe species formed during the different pretreatments. © 1994 Academic Press, Inc.

INTRODUCTION

Isomorphous substitution of Al^{3+} or Si^{4+} ions by Fe^{3+} ions in zeolite lattices (ferrisilicates) has been reviewed recently by Ratnasamy and Kumar (1). The substitution of Al^{3+} by Fe^{3+} leads to a reduction in the acidity of the system (2) while increasing the unit cell volume (3). It has been found that, generally, Fe^{3+} ions in zeolite lattices are less stable than Al^{3+} ions. At high temperatures especially in the presence of water they tend to leave the lattice positions and form bulk iron oxide species inside the zeolite channels (and on the external surface of the crystallites) (4), and undergo auto-reduction to Fe^{2+}, again leaving the lattice positions (5). Further, some of the ions leaving the lattice may also occupy charge-compensating positions on the lattice.

Ferrisilicate analogs of a number of medium and large pore zeolites, substantially free of Al^{3+} ions, have been synthesized and studied (1). The synthesis of the Fe analog of the zeolite beta has been reported by Kumar *et al.* (6). They have also confirmed the presence of Fe^{3+} in the tetrahedral positions in the lattice by a number of techniques including Mössbauer spectroscopy (7). Although these authors have shown the presence of Fe^{3+} (tetrahedral) ions in the lattice, their stabilities in reducing atmospheres (in the presence of hydrogen for example) is yet to be found out. This information is valuable in determining their catalytic usefulness when reducing agents like H_2 or hydrocarbons are present.

Although *in situ* Mössbauer spectroscopy is a unique tool to study the various forms of iron in zeolites, such studies on ferrisilicates have been scarce (8). We now report the characterization of the Fe species present in the ferri-beta (ferrisilicate analog of beta) zeolite under different treatments, including reduction in hydrogen and evacuation using *in situ* Mössbauer spectroscopy. The pretreated samples have also been characterized by other methods such as XRD, K^+ ion-exchange, and catalytic tests.

EXPERIMENTAL

Zeolite Synthesis

The synthesis of Fe-beta zeolite was carried out by mixing 0.62 g sodium hydroxide (AR, Loba Chemie, India), 0.46 g potassium hydroxide (AR, Loba Chemie, India), and 74 g tetraethylammonium hydroxide (Fluka, 40% aqueous solution). This solution was added to 24 g fumed silica (Sigma S-5005). The resultant mixture was stirred for 4 h to obtain a clear solution. A solution of 3.74 g ferric sulfate (GR, Loba Chemie, India) in 40 g distilled water was prepared. The silicate solution was slowly added to this solution over a period of 30 min to obtain a grey-coloured solution. This was crystallized at 413 K for 15 days. The final gel composition was

$$0.023(Na + K)_2O : 0.4\ SiO_2 : 0.0067\ Fe_2O_3 : 0.01\ (TEA)_2O : 8\ H_2O.$$

0021-9517/94 $6.00

The Si/Fe ratio of the crystalline solid (zeolite) was 26. The white solid product was centrifuged and washed until the pH of the washings was 7.5. The zeolite was highly crystalline and had an average crystallite size around 0.8 μm (SEM, Fig. 1). The sample is found to consist of uniform crystallites with well-defined edges without any extraneous matter. The intensity of the most intense peak (*hkl* = 302) was used for comparisons with other samples assuming the crystallinity of the above sample to be 100%.

The sample was then calcined by raising the temperature in 4 steps of 100 K to 753 K in a nitrogen atmosphere and holding the temperature for 12 h in air. The white solid was treated with a mixture of solutions of 0.1 *N* ammonium nitrate and ammonium hydroxide (pH = 7–8) for 5 h at 353 K and filtered. This procedure was repeated twice to obtain the ammonium form (sample B). Calcination of the NH_4^+ form in air at 723 K yielded the protonic form of the zeolite (sample C). The H-form was reduced in a flow of H_2 (1.2 liter h^{-1}) for 3 h at 523, 623, and 723 K to give samples D, E, and F, respectively.

Powder X-ray diffractograms were obtained on a Rigaku D MAXIIIVC spectrometer. The data processing was carried out using software available with the instrument. The exact position of the most intense peak (*hkl* = 302), viz., that at ca. $2\theta = 22.4°$ ($CuK\alpha$) was calculated using 5% Si as internal standard. The positional accuracy of the lines was better than $\pm 0.001°2\theta$.

Mössbauer Measurements

The Mössbauer measurements were carried out in the *in situ* cell described elsewhere (9) on samples of 400–600 mg pressed into a wafer. Spectra were collected in 512 channels, in a multichannel analyzer operating in multiscalar mode (constant acceleration). Spectra were fitted by Lorentzian curves; the reported isomer shift values are relative to α-iron. The estimated accuracy of the positional data is ±0.03 mm/s. All spectra were recorded at room temperature following the different treatments. *In situ* evacuation was carried out at 0.02 Pa in the Mössbauer cell, while hydrogen reductions were performed under continuous flow (ca. 0.3 liter h^{-1}, 100 kPa) of purified hydrogen in the same cell.

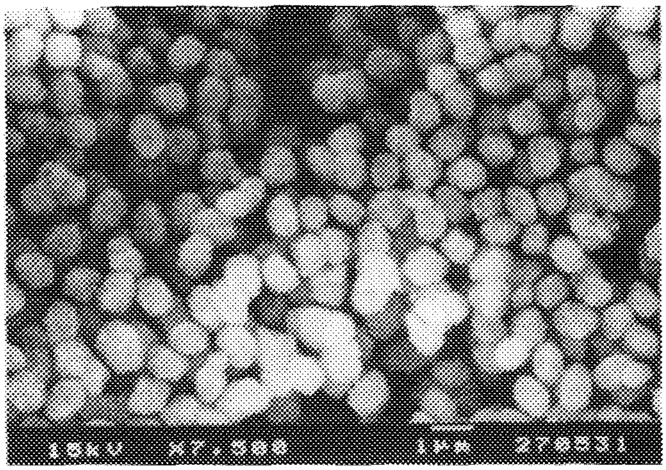


FIG. 1. Scanning electron micrograph of the Fe-beta (C/N form).

Ion-Exchange Studies

Ion-exchange measurements were performed by titrating the H-form of the zeolite (1 g) in 10 g distilled water with 0.05 *N* KOH up to pH = 8 and then stirring the mixture for 1 h, washing thoroughly and drying to obtain the K-form of the zeolite (10). The K-form of the zeolite was analyzed by atomic absorption spectroscopy to obtain the ion-exchange capacity.

Reaction Studies

Catalytic cracking of *n*-hexane and disproportionation of ethylbenzene(EB) were carried out on samples C–F in a fixed bed down flow reactor in a flow of purified nitrogen gas. During *n*-hexane cracking, the molar ratio of nitrogen to hexane (Aldrich > 99% pure) was 6. For EB, the molar ratio was 2. The weight hourly space velocity (WHSV) was kept at 1.76 h^{-1} and 1.73 h^{-1} for *n*-hexane and EB, respectively. The samples were analyzed in a HP1 (50 m × 0.2 mm × 0.5 μm film thickness, crosslinked methylsilicone gum) column in a gas chromatograph (Hewlett–Packard; 5880 A) equipped with a flame ionization detector.

RESULTS AND DISCUSSION

Mössbauer spectroscopy is a good tool for examining the various iron species present in zeolite samples. It is possible to distinguish not only between Fe^{2+} and Fe^{3+} species, but also between their coordination (tetrahedral or octahedral). The parameters used are the isomer shift IS (with reference to metallic iron) and the quadrupole splitting, QS. Using these parameters, earlier workers (7, 11–13) have been able to successfully identify and quantify the different Fe species in Fe-ZSM-5. We will now use these parameters to identify the species present in Fe-beta after different treatments.

Two series of *in situ* Mössbauer measurements were performed on the calcined (H-form) samples. The first set of experiments consisted of *in situ* evacuation of the sample C at 723 K (to estimate the extent of auto-reduction) followed by reduction at 623 and 723 K in hydrogen. In the second set of experiments, reduction in hydrogen was carried out at 523, 623, and 723 K without evacuation.

Mössbauer measurements were carried out *in situ* over the samples after the different treatments. The results of the experiments are presented in Table 1 and Fig. 2.

The components with lower isomer shift (IS) values have been assigned to Fe(III), those with values below 0.3 mm/s to Fe^{3+} in tetrahedral (Td), and those with values between 0.3 and 0.4 mm/s to Fe^{3+} in octahedral (Oh) coordination (13). The components with higher IS values belong to Fe(II), the Fe^{2+} (Td) being assigned values between 0.5 and 0.7 mm/s, and the Fe^{2+} (Oh) being assigned values between 0.8 and 1.1 mm/s (13). The quadrupole splitting (QS) values are also characteristic, though the limits for distinction of the various components are less strict. In general, an increasing symmetry of coordination of Fe(III) ions decreases QS, while the reverse holds true for Fe(II) ions (14).

The as-synthesized sample (sample A, C/N form) is found to possess only Fe^{3+} ions in tetrahedral locations (Table 1). Similar observations were also made by earlier workers (7) during their study of Fe-beta (C/N form) by Mössbauer spectroscopy. The NH_4^+ form obtained by calcination (753 K/12 h) of the C/N form and ammonium exchange (sample dried at 383 K) contains about 21% of the Fe^{3+} ions in octahedral (Oh) coordination, the rest being in tetrahedral (Td) coordination. On calcination at 723 K for 5 h, three different species, viz., Fe^{3+} (Td) (IS = 0.15 mm/sec), Fe^{3+} (Oh1) (IS = 0.33 mm/sec), and Fe^{3+} (Oh2) (IS = 0.37 mm/sec) can be identified based on the IS values. Apparently, some Fe^{3+} (Td) ions transformed into Fe^{3+} (Oh) on calcination of the NH_4^+ form. The transformation of Fe^{3+} (Td) into Fe^{3+} (Oh) on calcination has been reported by earlier workers (13) in the case of Fe-ZSM-5. For example, Meagher *et al.* (13) have reported 55% Fe^{3+} (Oh) ions in Fe-ZSM-5 (SiO_2/

TABLE 1

Results of the *in Situ* Mössbauer Measurements over Fe-Beta

Sample		Mössbauer parameters (mm/sec)		Nature of Fe		Relative spectral intensity[a] (%)
Code	Pretreatment	IS	QS	Oxidation state	Coordination	
A	C/N form	0.22	—	3+	Td	100
B	NH_4 form	0.21	—	3+	Td	79
		0.29	0.76	3+	Oh	21
C	B calcined at 723 K (12 h) (H-form)	0.15	0.56	3+	Td	27
		0.33	1.32	3+	Oh(1)	50
		0.37	0.68	3+	Oh(2)	23
		Series I				
D′	C evacuated (0.02 Pa) at 723 K	0.22	1.93	3+	Td	51
		0.63	0.89	2+	Td	42
		0.85	2.48	2+	Oh	7
E′	D′ reduced in H_2 at 623 K (3h)	0.19	1.46	3+	Td	41
		0.70	0.77	2+	Td	9
		1.02	1.94	2+	Oh	50
F′	E′ reduced in H_2 at 723 K (3h)	0.14	1.25	3+	Td	18
		0.68	0.65	2+	Td	8
		0.97	1.63	2+	Oh	42
		1.08	2.14	2+	Oh	32
		Series II				
D	C reduced in H_2 at 523 K (3h)	0.17	1.13	3+	Td	64
		0.51	0.91	2+	Td	19
		1.02	2.47	2+	Oh	17
E	D reduced in H_2 at 623 K (3h)	0.18	1.28	3+	Td	40
		0.68	0.62	2+	Td	8
		0.92	1.89	2+	Oh	35
		1.22	2.14	2+	Oh	16
F	E reduced in H_2 at 723 K (3h)	0.16	1.23	3+	Td	14
		0.67	0.57	2+	Td	8
		0.99	1.71	2+	Oh	45
		1.12	2.21	2+	Oh	33

[a] Parameter strongly related to concentration of the ions. Differences in Mössbauer–Lamb factors among the different species could influence the estimation of the concentrations based on the relative spectral intensities.

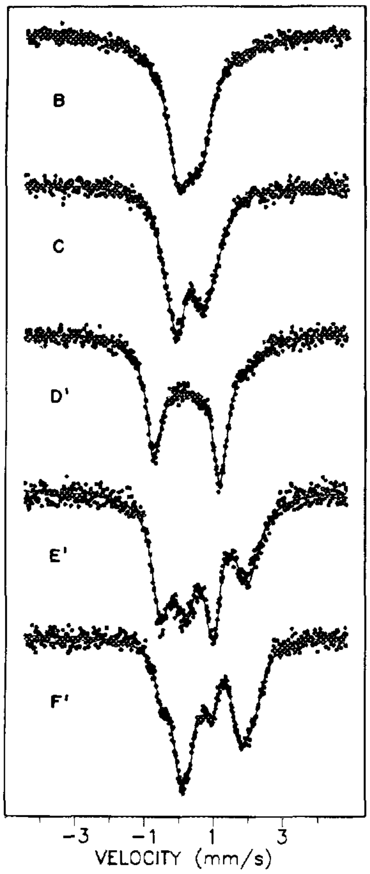


FIG. 2. Mössbauer spectra (*RT*) of Fe-beta samples after different pretreatments. (B) NH_4^+ form; (C) H^+ form (B calcined at 723 K, 5 h); (D') C evacuated at 723 K at 0.02 Pa; (E') D' reduced in H_2 (623 K, 3 h); (F') E' reduced in H_2 (723 K, 3 h).

Fe_2O_3 = 51) calcined at 773 K for 12 h. The NH_4^+-exchanged sample (B) and the H^+ sample (C, obtained after further calcination) were nearly as white as the as-synthesized sample, suggesting negligible amount of bulk Fe_2O_3 species in both the samples. Meagher *et al.* (13), however, did find a slight colour change (off-white) when they calcined a Fe-ZSM-5 sample at a higher temperature (773 K, 12 h). The colour difference is noteworthy because our sample contained more Fe^{3+} ions in octahedral coordination (Oh1 + Oh2). While Oh2 ions can be attributed easily to extra lattice iron species, the spectral parameters of the Oh1 species suggest that these species have a symmetry in between Td and Oh. The IS value is closer to Oh coordination but the QS value is too large for Fe^{3+} (Oh). Such large QS values have been reported earlier in Td coordinations (8). The above information and the lack of noticeable colour change suggest that the Oh(1) species are not extra lattice bulk iron oxide species. These probably arise from mixed Td/Oh coordination.

On evacuation of the calcined sample, the Fe^{3+} (Td) component increases to 51% (from 27%) while producing at the same time a large amount of Fe^{2+} ions through auto-reduction processes. Such auto-reduction of Fe^{3+} in zeolites has already been reported by earlier workers (15). An increase in the Fe^{3+} (Td) content is also observed when the calcined sample is reduced at 523 K. The question is: how do evacuation and H_2 reduction increase the amount of Fe^{3+} (Td) species? When Fe-beta was calcined in air at temperatures exceeding 773 K, a light brown colouration suggesting the presence of bulk Fe_2O_3 was observed by us. This shows that bulk Fe_2O_3 is formed only when the calcination temperature exceeds 753 K. It appears, therefore, that the Fe^{3+} (Oh1) species observed by us on calcination at a lower temperature (723 K), which revert (partly) into Fe^{3+} (Td) on evacuation or mild reduction, are probably well-dispersed Fe^{3+} ions still attached to the lattice (see later). An interesting observation (Table 1) is that both sets of samples reduced above 623 K (E, E' and F, F') possess a similar distribution of the different Fe^{3+} and Fe^{2+} ions irrespective of the evacuation treatment.

The ion-exchange capacity of the samples and their catalytic activities are also presented in Table 2. The data are plotted in Fig. 3 against the variation in *d* value of the 2θ = 22.4° peak. An increase in *d* value indicates expansion of the lattice due to the presence of the bulkier Fe^{3+} ions in the lattice. A reasonable linearity in the *d* value variation with ion-exchange capacity is noted (Fig. 3). Further, except for the calcined (H form) sample, there appears to be again a linear correlation between the *d* values and the Fe^{3+} (Td) species estimated by Mössbauer spectroscopy. This suggests that the Fe^{3+} (Td) species estimated by Mössbauer are in the lattice and possess ion-exchange properties. Tentative structures for the Fe^{3+} species present in the different samples are given in Scheme 1.

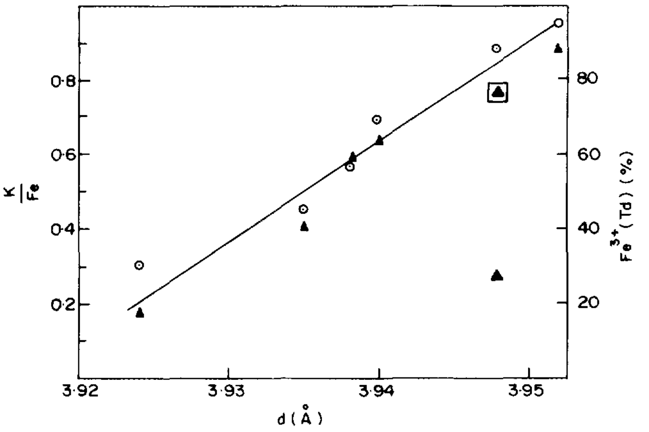


FIG. 3. Correlation between interplanar spacing (*d* value of 2θ = 22.4° peak, Cu*Kα*) and Fe^{3+} ions in lattice. (⊙) Ion-exchange capacity (K/Fe); (▲) Fe^{3+} (Td) from Mössbauer spectroscopy; ▲ calcined sample C (Fe^{3+} (Td) + Fe^{3+} (Oh1)).

TABLE 2

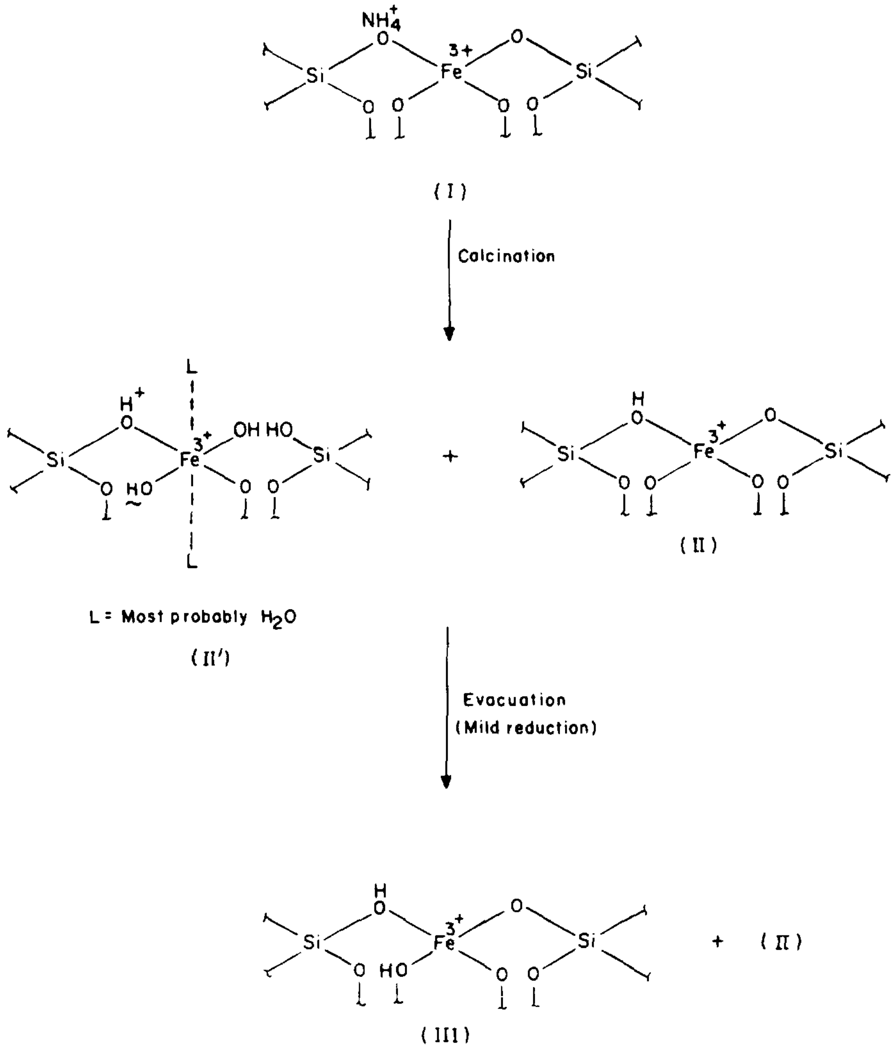
Physicochemical Characterization and Catalytic Activities of the Zeolites Used in the Study

Sample (code)	Colour	d(Å) of 22.4° peak in XRD[a]	Linewidth (°)	Relative crystallinity[b]	Ion-exchange capacity (K/Fe)	Fe^{3+}-Td (Mössbauer)[c] (%)	Catalytic activity conversion (wt%)	
							n-hexane	Ethylbenzene
NH_4 form (B)	White	3.952	0.04	0.96	0.96	79	—	—
H form (C)	White	3.948	0.09	0.92	0.89	27 (50)	16.88	29.97
Evac. 723 K (D')	Yellowish brown	3.938	0.08	0.79	0.57	51	—	—
Red. 523 K (D)	Light brown	3.940	0.08	0.77	0.69	64	13.05	26.79
Red. 623 K (E)	Light brown	3.935	0.08	0.59	0.45	41	6.08	18.00
Red. 723 K (F)	Dark brown	3.924	0.08	0.53	0.31	18	2.96	10.87

[a] *hkl* = 302; maximum deviation in values ±0.002° 2θ.

[b] Reference: C/N form = 1.

[c] Values in brackets refer to Fe^{3+} (Ohl); these species also possess ion-exchange capacity.



SCHEME 1

TABLE 3

Catalytic Studies over Fe-Beta[a]

	n-hexane cracking				EB transformation				
Sample code	Conv. (wt%)	C_6	iso-C_6	Others	Conv. (wt%)	C_5 gases	Bz[b]	DEB[c]	Other aromatics[d]
B	16.88	14.26	0.82	1.40	29.97	1.37	21.90	0.83	5.87
C	13.05	10.69	0.57	1.59	26.78	1.57	18.73	0.79	5.69
D	6.08	4.29	0.45	1.39	18.0	1.43	11.75	0.76	4.06
E	2.96	1.45	0.46	1.05	10.87	0.92	6.60	0.77	2.58

[a] Reaction conditions: Temperature = 723 K; Pressure = atm.; WHSV (h^{-1}) = 1.76 and 1.73 for *n*-C_6 and EB; N_2/HC (mole) = 6 and 3 for *n*-hexane and EB.

[b] Benzene.

[c] Diethylbenzenes.

[d] Mostly ethyl toluenes, cumene, and styrene.

Species I and II are typical cases expected to be present in zeolite (tetrahedral) lattices. Species II′ has Fe^{3+} in an octahedral coordination and is still connected to the zeolite lattice by two O bridges. The exact number of connectivities in these species could, however, be different from what has been depicted. When all the O bridges are broken, a discrete Fe^{3+} ion is created; these ions can migrate freely and, when enough such ions come together, form bulk Fe_2O_3 (small crystallites). We propose that species II′ is the same as the Fe^{3+} (Oh1) species produced on calcination of the NH_4^+ form at 723 K. The tetrahedral feature of Fe^{3+} (Oh1) as suggested might originate from the four covalent linkages with O atoms while the octahedral feature is a result of the ligands (L) forming a "second coordination sphere" as depicted in the scheme. The restoration of a third oxygen bridge connecting the zeolite lattice via dehydration and removal of ligands (evacuation/reduction) will lead to the transformation of these species(II′) into Fe^{3+} (Td) (species II). Species II′ also possesses the ion-exchange property. The lone point (corresponding to the H form) found to deviate in Fig. 2 contains these Fe^{3+} (Oh1) species. If we assume that these species have also taken part in the ion exchange, then this point also will be closer to the straight line (Td + Oh1 = 77%) (point inside box). The NH_4^+ sample was dried at 383 K and hence not fully "dry." The sample contained a significant amount of moisture along with NH_4^+ ions. During calcination (723 K), the moisture liberated could have hydrolyzed the M–O–M linkage leading to the formation of the Fe^{3+} (Oh1) species(II′). Higher temperatures (>773 K) or larger amounts of moisture would, however, lead to greater hydrolysis and dislodging of the Fe^{3+} from the lattice, thereby "demetallizing" the zeolite and causing the formation of bulk iron oxide species.

The results also suggest that the Fe^{2+} species (both Td and Oh) produced during evacuation or H_2 reduction do not possess ion-exchange properties and are presumably outside the zeolite lattice. The Fe^{2+} (Td) species are probably single ions outside lattice positions in the center of secondary building units as suggested by earlier workers (16). The concentration of Fe^{2+} (Td) decreases on increasing the temperature of reduction, while the Fe^{2+} (Oh) species, increases (Table 1). The latter component might be located either in the structural channels or around the lattice defects formed by removal of lattice iron during reduction. These two site assignments may correspond to the two distinct Fe^{2+} (Oh) species detected after 723 K reduction.

The results of the catalytic experiments are also presented in Table 3. It is again observed that there is a definite direct relationship between the *n*-hexane cracking and EB conversion activities and Fe^{3+} (Td) ions estimated by Mössbauer and ion-exchange data. This relationship confirms that catalytic activity is a result of the acid centers associated with the Fe^{3+} (Td) ions. In the ethylbenzene reaction, it is noted that the yield of diethylbenzenes does not decrease significantly when the acidity of the sample (as measured by ion-exchange capacity) decreases in the samples. However, the yield of benzene (mostly from the cracking of EB) decreases nearly linearly with the decrease in ion-exchange capacity, suggesting that the cracking reaction is more dependent on the acidity of the sample.

CONCLUSIONS

1. Calcination of Fe-beta leads to the possible formation of mixed tetrahedral–octahedral Fe^{3+} (Td/Oh) (defect) sites with ion-exchange capability.
2. On evacuation at 723 K, auto-reduction of Fe^{3+} to Fe^{2+} takes place. Further, a fraction of the defect sites Fe^{3+} (Td/Oh) transform into Fe^{3+} (Td) presumably "reverting back" to lattice positions. A similar transformation also occurs on mild reduction with H_2 (523 K).

3. Reduction of Fe-beta leads to the loss of Fe^{3+} from lattice positions and the formation of Fe^{2+} (Td and Oh) ions.

4. A strong correlation is demonstrated between cracking activity and the amount of exchange sites in the samples.

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