STRUCTURE AND CATALYTIC PROPERTIES OF FERRISILICATE ZEOLITES OF THE PENTASIL GROP

P. RATNASAMY, R. B. Borade, S. Sivasanker, V. P. Shiralkar, S. G. Hegde, National Chemical Laboratory, Pune 411008, India.

ABSTRACT

A ferrisilicate pentasil zeolite was synthesised. Its structure was characterised by XRD, ESCA, Mössbauer, ESR and IR spectroscopy, magnetic susceptibility and adsorption techniques. The as-synthesised zeolite contains Fe^{3+} in (1) isomorphous substitution in lattice positions, (2) cation exchange positions and (3) oxide/hydroxide phases. On treatment with nitric acid, the Fe^{3+} ions in non-lattice positions are extracted out. The product is an iron zeolite containing Fe^{3+} and Si^{4+} ions in tetrahedral lattice positions. The temperature-programmed desorption of NH_3 from this zeolite reveals the absence of very strong acid sites in it. Consequently, its catalytic property in the isomerisation of xylenes is different from that of the aluminium analog.

INTRODUCTION

The discovery, manufacture and industrial applications of synthetic crystalline aluminosilicate zeolites has been one of the significant developments in catalysis during the past half century. We now report the synthesis, physicochemical and catalytic properties of a ferrisilicate pentasil zeolite containing both iron and silicon in lattice positions. Even though there are references in the patent literature [1-4] on the

synthesis and catalytic properties of these materials, there are no detailed journal reports on this system. Marosi et al [1,2] claimed the preparation of zeolites with ZSM5 topology and containing iron. No experimental data were provided regarding the location of iron [5].

EXPERIMENTAL

Materials : The iron zeolites (FeZ) were prepared using various sources of Fe, Si, alkali as well as different organic templates [6]. A typical procedure is given below. To 20 g of sodium silicate (8.2% Na_2O, 27.2% SiO_2, 64.6% H_2O)10 ml of water is added to constitute solution A. 2.5 g of tetrapropylammonium bromide is dissolved in 10 ml of water to give solution B. 0.54 g of ferric sulphate (31.2% Fe_2O_3 is added to enough water at 323 K to yield a clear solution C. 1.76 g of H_2SO_4(98%) is diluted in 15 ml of solution to give solution D. Solution B is added to solution A with stirring.Solution C is then added to the mixture with stirring. Solution D is finally added to the resulting mixture dropwise with constant vigorous stirring. A solid gel is formed whose pH is about 10.2. The slurry containing the gel is heated at 423 K in an autoclave under autogenous pressure for 24 hrs. The autoclave is then quenched in cold water. The solid product is filtered, washed with hot water till the filtrate is free from sulphate ions and dried at 393 K for 12 hrs. The material was then calcined in a static air oven at 823 K for 8 hrs to remove the organics. The acid form of the zeolite was obtained by ion exchange (twice) with 5 N ammonium nitrate solution at 363 K for 15 hrs followed by drying and calcination. The non-zeolite iron was finally

extracted out by treatment with nitric acid. The purity of all the reagents and chemicals ued for the adsorption, TPD and catalytic experiments was better than 99%.

Procedures : The instruments and procedures for measuring the X-ray diffraction pattern, temperature-programmed desorption of NH_3, adsorption isotherms and catalytic properties of pentasil zeolites were similar to those described earlier [7-11] for HZSM5 samples. The XPS measurements were performed [12] with a commercial XPS spectrometer (Vaccum Generators, ESCA 3 MK II). The experimental techniques including the calibrations procedures had been described earlier [12].

The ESR spectra were recorded on a Brucker E.R. 100 D spectrometer, at 298 K. The spectrometer was operated at X-band frequency (9.6 GHZ) and calibrated with diphenyl picryl hydrazine (DPPH). The Mössbauer spectra were recorded by Dr. B. Clausen (Haldor Topsoe, Denmark) using a source of ^{57}Co in Rh matrix (Amersham) with the spectrometer in the constant acceleration mode. The spectrometer was calibrated with a thin (12.5 μm) foil of α- Fe at room temperature. Isomer shifts are given relative to the centroid of this spectrum. 125 mg/cm of sample was used. The magnetic susceptibility data were obtained by the Faraday method at 298 K.

RESULTS AND DISCUSSION

1. Composition and crystal structure : The unit cell composition of a typical sample of iron zeolite (Fe2) in the anhydrous acid form was $Na_{0.04}H_{2.55}[(SiO_2)_{93.41}(FeO_2)_{2.59}]$. Its XRD pattern, that of an aluminium pentasil zeolite ZSM5(Al)

and silicalite are shown in Fig. 1. From the similar X-ray patterns, it is concluded that all the samples of Fig. 1 are pentasil zeolites. This is further supported by the IR framework vibration frequencies of FeZ (Table 1) which are similar to those for HZSM5 [7]

Table 1 : IR frequencies (cm^{-1}) of FeZ and HZSM5(Al)

FeZ : 455,550,590,620,678,730,800,870,888,1040,1100,1230

HZSM5(Ref.7): 450,540,590,620,680,720,790,840,1075,1220

2. Oxidation state and location of iron :

A XPS : That the iron ions in FeZ are in the trivalent state and are indeed situated in lattice positions (and not occluded in the pores) is indicated by the XPS data in Fig. 2, which presents the XPS spectra of iron and oxygen in FeZ (Fig.2) and in a sample of silicalite containing occluded Fe_2O_3. The latter was prepared by impregnation of silicalite with $Fe(NO_3)_3$ followed by drying and calcination. The binding energies of the Fe_{2p} level in the samples (taking a value of 103.3 eV for the Si_{2p} level as the internal standard) were 711.6 (FeZ) and 711.0 (Fe-Sil) indicating Fe^{3+} in both the materials. A $2_{p3/2}$ - $2_{p1/2}$ split-ting of 14.0 eV was observed for both the samples. These results agree with those of Mikusik et al [13] who found a value of 711.1 eV for Fe_2O_3 and 710.5, 711.7 for Fe^{3+} ion exchanged into HY zeolite. However, while only one O_{1s} peak (due to the zeolite lattice oxygen) is observed for FeZ, two peaks at 531.5 and 529.1 eV are seen (Fig. 2) in the case of FeSil. While the peak at 531.5 eV, corresponds to the zeolite lattice oxygen, the other corresponds to the oxygen associated with the occluded Fe_2O_3

phase as could be verified with pure Fe_2O_3 . Stencel et al[14], for a sample of ZSM5 containing occluded Fe_2O_3 had also observed two O_{1s} peaks at 532 and 529 eV, corresponding to oxygen in the zeolite and Fe_2O_3 respectively.

B Mössbauer Spectra : The Mössbauer spectra of FeZ (sodium form) at 300 and 80 K are shown in Fig. 2. These had been computer analysed as a two line and a six-line spectral component to represent the quadrupole doublet and the magnetically split spectrum, respectively. The values of δ (the isomer shift with ref.to Fe) and Δ (the quadrupole splitting) of the quadrupole doublet are given in Table 2. These are typical of Fe^{3+} in high spin state. The Mössbauer spectra of iron ion-exchanged into NaZSM5 (Fig. 5 of ref. 15) are completely different from Fig, 3, supporting our view that Fe^{3+} ions in our samples are in lattice positions and not as countercations. In Ref. 15, iron was present as (1) Fe^{2+} octahedrally coordinated to water molecules (δ = 1.37, Δ 3.27), (2) Fe^{2+} in distorted tetrahedral coordination (δ = 0.75, Δ = 1.28) and (3) Fe^{2+} in tetragonally distorted octahedral symmetry (δ = 1.30, Δ = 3.72). None of these species are present in our sample.

Table 2 : Mössbauer parameters (quadrupole doublet) of of iron zeolite (Na form)

Temp. (K)	δ (mm/s)	Δ (mm/s)	Rel area (%)
300	0.33 + 0.02	8.85 + 0.02	90
80	0.42 + 0.03	1.05 + 0.03	74

In addition to the lattice Fe^{3+}, our spectra (Fig. 3) indicate the presence of small occluded particles of Fe_2O_3 or Fe_3O_4 also. These species, responsible for the magnetically split six line component, are removed by acid extraction perocedures.

C ESR Spectra : The ESR spectra of the as-synthesised zeolite gave evidence for the presence of at least four different kinds of iron sites with g = 4.3, 2.3, 2.0 and 5.3 respectively (Fig. 4). The resonance at g = 4.3 was attributed to high spin Fe^{3+} in the lattice [16] and/or Fe^{3+} in rhombohedrally distorted tetrahedral complexes in cation positions [17]. Since the signal at g = 4.3 was not significantly affected by the level of hydration, treatment in hydrogen or with HNO_3, it was concluded that, in our case, it arises mainly from the presence of Fe^{3+} in lattice. Treatment with HNO_3 decreased drastically the intensity of the signals at g = 2.3, 2.0 and 5.3 indicating that they are due to iron in nonlattice positions. The signal at g = 2.3 is atributed, in agreement with Wichterlova [16], to Fe^{3+} ions in occluded oxide and hydroxides. Similarly, the weak signal at g = 2.0 is due to hexacoordinated Fe^{3+} aquo/oxo complexes located in the cationic sites [16]. The signal at g = 5.3 arises probably from highly distorted tetrahedral complexes of Fe^{3+}.

D Magnetic Susceptibility : The magnetic susceptibility values (cgs units/g) for FeZ and a sample of silicalite containing an equal amount of Fe (as Fe_2O_3) were 4.9 and 3.2 x 10^{-6}, respectively, indicating the larger dispersion of Fe^{3+} in the former (at lattice sites) compared to the latter.

3. Adsorption Properties : The adsorption of H_2O and hydrocarbons in FeZ is shown in Table 3. The values are comparable to those for HZSM5 (Al) published earlier [7]. The shape selective behaviour of FeZ is seen from the large differences in the adsorption of n-hexane and its branched isomers (Table 3).

Table 3 : Adsorption properties of FeZ (Na form)

Absorbate (297 K, Sat.Vap.)	Kinetic diameter, A	Amount adsorbed Molecules/unit cell
H_2O	2.65	26.0
n-Hexane	4.30	7.7
2-Methyl Pentane	5.5	5.8
Cyclohexane	6.0	2.7
2,3-Dimethyl butane	6.1	3.4

4. Acidic Properties : The TPD spectra of NH_3 from FeZ, HZSM5 and silicalite are shown in Fig. 5 (curves denoted by Fe, Al and Si, respectively). The peak at 673 K in HZSM5, due to strongly adsorbed NH_3, is shifted to 610 K in FeZ, indicating that SiOHFe Brönsted acid sites are weaker than those of SiOHAl. The broad, weak peak at 540-673 K in silicalite is due to the presence of Al impurities.

5. Catalytic Properties : In the catalytic conversion of C_8 aromatics over FeZ and HZSM5 (Table 4), the major difference is that at similar conversion of ethylbenzene (EB) and para-xylene approach to equilibrium (PATE), the selectivity of FeZ is higher than that of HZSM5 (lower xylene loss).

Table 4 : Comparison of FeZ and HZSM5 (Al)

Conditions : 713 K, atm.pr., WHSV = 15 hr , H /Oil = 0

Product distribution(wt.%)	Feed	FeZ	HZSM5(Al)
C Aliphatics	2.9	2.7	2.1
Benzene	0.6	9.0	9.9
Toluene	3.0	4.0	5.1
Ethyl benzene	26.5	13.7	14.6
p-Xylene	7.4	14.5	14.4
m-Xylene	55.0	40.1	38.8
o-Xylene	4.6	12.2	12.6
C_9^+ Aromatics		3.8	5.6
EB Conversion % wt.		48.3	45.4
PATE		90.0	94.0
Xylene loss		0.2	4.2

ACKNOWLEDGEMENT : We thank Drs. S. Badrinarayanan and B. Clausen for the XPS and Mössbauer data, respectively.

REFERENCES

1. Marosi, L., Stabenow, J., Schwarzmann, M., Ger. 2,831,611.

2. Marosi, L., Stabenow, J., Schwarzmann, M., Ger. 2,831,630.

3. Dwyer, F., U.S. 3,941,871.

4. Kouwenhoven, H.W., Stork, W. H. J., U.S. 4,208,305.

5. Barrer, R. M., Hydrothermal Chemistry of Zeolites, AP, London, 1982, p. 292.

6. Borade, R.B., Kulkarni, S.B., Hegde, S.G., Kotasthane, A.N., Shiralkar, V.P., Ind. 275/DEL/83.

7. Kulkarni, S.B., Shiralkar, V.P., Kotasthane, A.N., Borade, R.B., Ratnasamy, P., Zeolites, 4, 313 (1982).

8. Babu, G.P., Hegde, S.G., Kulkarni, S./B., Ratnasamy, P.,

J. Catal. 81, 471 (1983).

9. Chandavar, K.H., Kulkarni, S.B., Ratnasamy, P., Appl. Catal., 4, 287 (1982)

10. Borade, R.B., Hegde, S.G., Kulkarni, S.B., Ratnasamy, P., Appl. Catal., 13, 27 (1984).

11. Meshram, N.R., Hegde, S.G., Kulkarni, S.B., Ratnasamy, P., Appl. Catal., 8, 359 (1983).

12. Badrinarayanan, S., Hegde, R.I., Kulkarni, S.B., Ratnasamy, P., J. Catal. 71, 439 (1981).

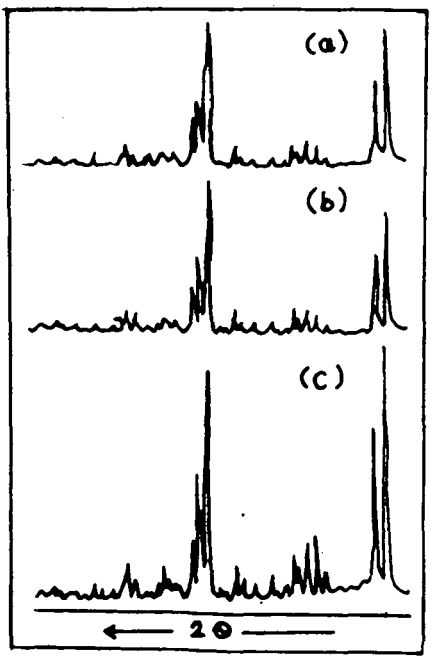
13. Mikusik,P., Juska, T., Novakova, J.,Kubelkova, L., Wichterlova, B., J. Chem. Soc. Faraday Trans. I.,77, 1179 (1981).

14. Stencel, J. M., Diehl, J.R., Doublas, L. J., Spitler, C.A., Crawford, J.E., Melson, G.A., Colloids and Surfaces, 4, 331(1982).

15. Petrera, M., Gennaro, A., Gherardi, P., Gubitoza, G., Pernicone, N., J. Chem. Soc. Faraday Trans. I., 80, 709 (1984).

16. Derouane, E.G., Mestdagh, M., Vielvoye, L., J. Catal. 18, 90 (1970).

17. Wichterlova, B., Zeolites, 1, 181 (1981).



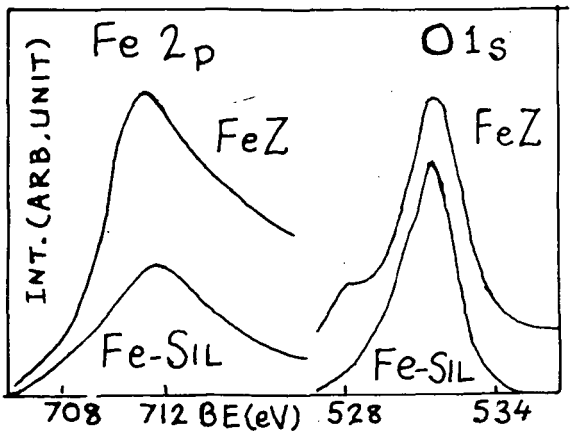


Fig.2: XPS of FeZ and Fe-Silicalite.

Fig.1: XRD Spectra of FeZ, HZSM5 and silicalite (curves a-c).

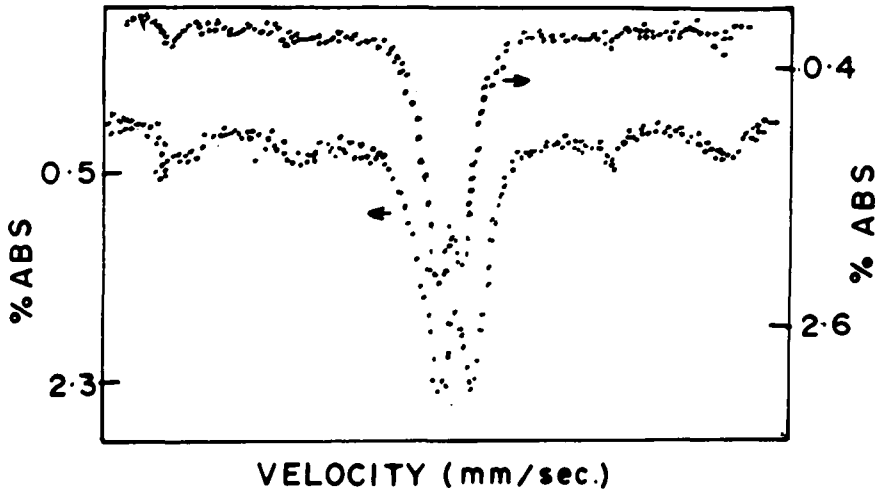


Fig 3:Mössbauer spectra of FeZ at 300(top) and 80K (bottom).

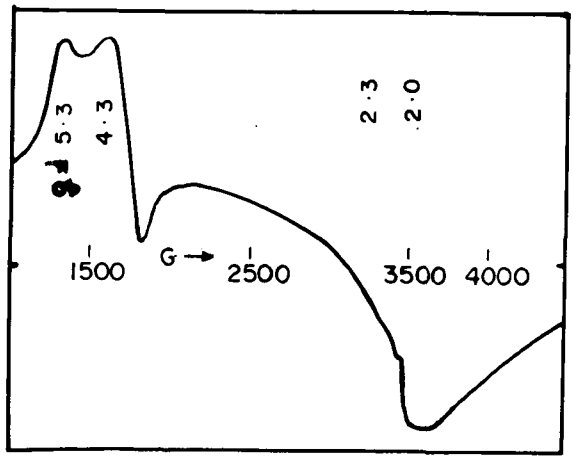


Fig. 4 : ESR Spectra of FeZ .

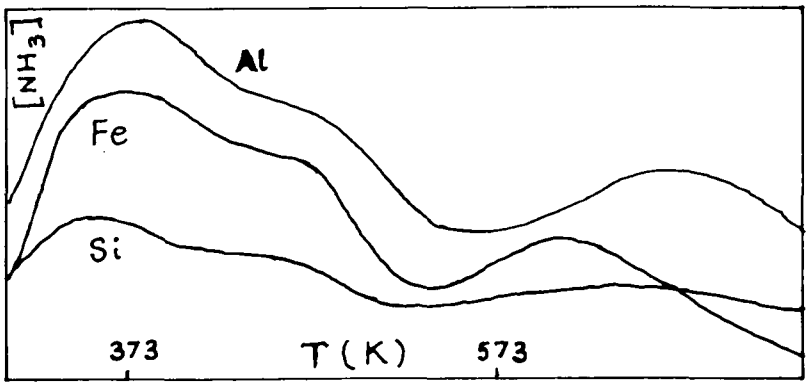


Fig.5 : TPD(NH_3) spectra of HZSM5(Al), FeZ(Fe) and silicalite(Si).