

ELECTRON SPIN RESONANCE INVESTIGATION OF  $Fe^{3+}$  IONS IN FERROSILICATES OF THE ZSM-5 TYPE

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Toernooiveld, 6525 Ed Nijmegen, The Netherlands**Abstract**

The redox behavior of  $Fe^{3+}$  located in ZSM-5 Zeolite framework, in cationic sites and in the form of including hydroxy-oxidic compounds is investigated by means of electron spin resonance spectroscopy. The spectra shows an isotropic signal arises at  $g = 4.3$ . This signal is due to  $Fe^{3+}$  situated in the framework. The intensity of the resonance at  $g = 4.3$  depends on the amount of  $Fe^{3+}$  in the framework which increases with the concentration of iron in the sample. Resonances at  $g = 2.6$ ,  $g = 2$ ,  $g = 2.3$ ,  $g = 2.1$ ,  $g = 2.7$  and  $g = 1.8$  can be attributed to iron compounds precipitated in the cavities of zeolites during the synthesis process.

**Introduction**

Natural and synthetic zeolites are widely employed in industry because of their desirable physico-chemical properties and relatively low cost. Apart from applications as selective adsorbents and catalysts, zeolites are used as additives to detergents, animal feed or fertilizer due to their efficient ion exchange properties[1-4]. More recently, particular synthetic zeolites are also used in the catalytic conversion of methanol to olefins and hydrocarbons (Mobil Process).

A number of investigations has been devoted to the study of the electron spin resonance (ESR) of iron ions as impurities in different kinds of zeolites. In these studies, the characteristic feature of the ESR spectra of  $Fe^{3+}$  ions is the appearance of three absorptions peaks with  $g_{eff} = 4.3$  (sharp signal),  $g_{eff} = 2.7$  and  $g_{eff} = 2$  (both broad signals). McNicol and Pott[5] have shown unambiguously that the  $g_{eff} = 4.3$  signal observed in faujasite and mordenite is due to  $Fe^{3+}$  situated in the framework. In the same work, and in an earlier study by Singer and Stamires[6], broad electron spin resonance signals were also observed in heated  $NH_4$  zeolites, they were attributed to  $Fe_2O_3$  or  $Fe(OH)_3$  species precipitated in the cavities during the deammoniation process third possibility is that  $Fe^{3+}$  cations (presumably



### Method 2

Two-hundred milligrams of zeolite were added to 10 ml distilled water and 2 ml 10% NaCl solution in a 25 ml flask. After addition of 100 mg  $\text{Na}_2\text{Si}_2\text{O}_7$ , the mixture was heated for 15 minutes at 70°C and filtered, the remaining solid was dried in air. This procedure was repeated three times.

### Instrumental techniques

Res measurements were made on a X-band E-12 Varian spectrometer, using 100 kHz modulation at 4.2 K using a liquid He cryostat especially designed for low-temperature work.

### Experimental results

In Figs. 1 and 2, the ESR spectra measured at 4.2 K are presented for sample 1 (Si/Fe = 10.7) and sample 2 (Si/Fe = 6.6), respectively, for the hydrated and the dehydrated states.

#### Sample 1

The hydrated sample shows a narrow peak (derivative linewidth 100 gauss), at  $g = 4.3$  and broad signals at  $g = 2.6$  (weak) and  $g = 2$  (strong). On dehydrating the spectrum changes drastically. A new peak appears at  $g = 7.7$ , the peak at  $g = 4.3$  is still observed and at higher magnetic fields absorption occurs over a large field range.

#### Sample 2

The hydrated sample shows a very weak signal at  $g = 4.3$  and broad and intense signals at  $g = 2.7$  and  $g = 1.8$ . On dehydration also this spectrum changes drastically. The weak signal at  $g = 4.3$  can still be observed, but strong resonance signals are now seen at  $g = 2.3$  and  $g = 2.1$ .

Exposure of the dehydrated samples for 24 hours to water in a closed system yielded the spectra of the hydrated samples again.

### Discussion

Several authors have shown[11-14] that the ESR spectra of high spin  $\text{Fe}^{3+}$  (ground state  $^6S_{5/2}$ ) can be explained by the spin hamiltonian

$$H = D(S_z^2 - 1/18(S+1)) + F(S_x^2 - S_y^2) + g_0^R R.S$$



The first term, the crystal field term, dominates over the Zeeman term ( $g_0$  is the isotropic  $g_{J0}$  value). If  $Q/E = 1/3$  it has been shown that an isotropic signal arises at  $g = 3Q/7 = 4.3$ . Our samples show this signal which is very characteristic for  $Fe^{3+}$  in a distorted tetragonal site of symmetry  $C_{2v}$ . Nicol and Pott[5] proved that it can be ascribed to  $Fe^{3+}$ , situated in the silicon-oxygen framework. It has also been observed in iron containing glasses, where  $Fe^{3+}$  ions replace the  $Si^{4+}$  ions in the tetrahedral network[11]. In accordance with the Si/Fe ratios of the samples the signal at  $g = 4.3$  is more intense in the spectrum of sample 1 (Si/Fe = 10.7) than in the spectrum of sample 2 (Si/Fe = 6.6). From the observed resonances of lower  $g$  values it is also clear that most of the iron atoms are not built in the framework. According to the work of Derouane et al[7], these resonances can be attributed to iron compounds precipitated in the pores during the synthesis process and to iron atoms situated at so called exchange cation positions. With the extraction procedures described in the experimental part we were unable to remove these iron atoms from the material.

The changes in the spectra on dehydration is interesting. Analogous phenomena were observed by Veeman et al[15] in the  $^{23}Na$  and  $^{27}Al$  NMR spectra of ZSM-5 zeolites. These authors showed that on dehydration the quadrupole interaction of Na and Al increased so much that the NMR signals broadened beyond detection. In the ESR spectra this manifests itself in different crystal field parameters, leading to changes in the spectra.

#### References

1. P. Berth, G. Isakbi, E. Schmadel, M.J. Schwuger and C.H. Knauch, *Angew. Chem. Int. Ed.* **14** (1975) 94.
2. M.J. Schwuger and H.G. Smolka, *Colloid and Polymer Sci.* **254** (1976) 1062.
3. *Anon. Chem. Eng. News*, May 22 (1978) 11.
4. *Anon. Chem. Eng. News*, Sept. 20 (1980) 705.
5. B.D. McHicol and G.T. Pott, *J. Catal.* **25** (1972) 225.
6. I.S. Singer and D.N. Stamiris, *J. Chem. Phys.* **42** (1965) 3299.
7. E.J. Derouane, M. Mesdagh and L. Vielvoys, *J. Catal.* **33** (1974) 169.
8. Eleonora Taif et al. XXIIIrd Congress Ampère on Magnetic Resonance and Related Phenomena, Proc. September 1984, The University of Zürich, Switzerland.
9. L.C.J. Bart, N. Burriesci, F. Carati, M. Petrona and C. Zepf, *Zeolites* **3** (1983) July.
10. J.P. van den Berg, Thesis Eindhoven, The Netherlands 1981; P.B. Weisz, *Pure and Appl. Chem.* **52** (1980) 2091.
11. E. Cantner, Jr., G.S. Newell, W.C. Hutton and C.P. Slichter, *J. Chem. Phys.* **32** (1960).
12. J.B. Griffith, *Adv. Phys.* **6** (1964) 213.