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The Mössbauer Effect and Magnetometric Investigations of Iron-Doped Sodium A-Type Zeolite

By

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The properties of zeolites are strongly influenced by impurities, mainly iron ions, which are always present in commercial zeolites. The impurity ions are thought to take the exchange sites /1 to 8/, to substitute Al/Si ions in a zeolite crystal lattice /8, 9/, or to be present in the form of iron oxides /8, 10/.

The purpose of this paper is to present the results of investigations of iron-doped sodium A-type zeolite performed with the Mössbauer effect and the magnetic susceptibility methods. The iron irons were introduced into zeolite, not by the commonly used exchange method, but during the preparation process which is thought to enable ferric ions to take Al/Si positions in the zeolite crystal lattice.

The sodium A-type zeolite hydrated, dehydrated, and rehydrated sample was the subject of Mössbauer effect investigations. Dehydration was performed at 623 K in vacuum for 12 h in a thin-wall quartz cell. Rehydration of the sample took place after the quartz cell was opened. The preliminary results of Mössbauer effect investigations and experimental details were published in /11/.

The spectra for the hydrated sample were taken at 293, 78, and 4.2 K, whereas the spectra for the dehydrated one were taken at 293 and 78 K. The rehydrated sample was measured only at 293 K. For a given spectrum the ^{57}Co(Cr) source and the absorber were at the same temperature. Two of these spectra are shown in Fig. 1.

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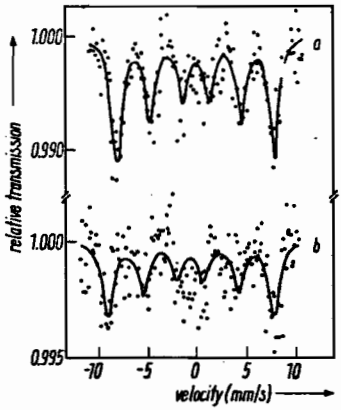

Fig. 1. Mössbauer spectra for a) hydrated sample at 4.2 K, b) dehydrated sample at 78 K

The iron ions introduced into zeolite during the preparation process behaved quite differently from those introduced by the ion exchange method /5/. For the hydrated sample a quadrupole doublet was observed at 293 K which had a quadrupole splitting $\Delta E = (0.71 \pm 0.02)$mm/s and isomer shift (relative to Fe metal) $\delta = (+0.32 \pm 0.02)$mm/s. The lines of the quadrupole doublet became broadened at 78 K and the Zeeman splitting (Fig. 1a) appeared at 4.2 K from which $H_{eff} = (494 \pm 10)$kOe was calculated. The rehydrated sample gave at 293 K a quadrupole doublet with $\Delta E = (0.98 \pm 0.02)$mm/s and $\delta = (+0.26 \pm 0.02)$mm/s but at 78 K it showed a Zeeman splitting (Fig. 1b) with $H_{eff} = (515 \pm 10)$kOe. The spectrum of the rehydrated sample contained at 293 K the doublet with $\Delta E = (0.84 \pm 0.02)$mm/s and $\delta = (+0.27 \pm 0.02)$mm/s. The quadrupole splitting and the isomer shift were found to be almost temperature independent and practically not influenced by the dehydration process. The correlation of the isomer shift and the quadrupole splitting (Duncan diagram) indicates the existence of ferric ions in the investigated sample. No traces of a second phase have been observed with the X-ray diffraction method.

There are two possible explanations of the obtained Mössbauer spectra. The first is based on the assumption that ferric ions are placed on the Al/Si positions of the zeolite crystal lattice /8, 11/.

The second explanation involves the existence of ultra fine iron-oxygen superparamagnetic clusters in the investigated sample. They might be produced during the preparation process of zeolite and due to their small sizes are not observed in the X-ray analysis. The parameters describing our Mössbauer spectra are similar to those obtained for superparamagnetic α-Fe_2O_3 particles of average diameter less than 100 Å/12/.

In order to distinguish between these two interpretations we performed the magnetic susceptibility measurements for the hydrated and dehydrated samples using the

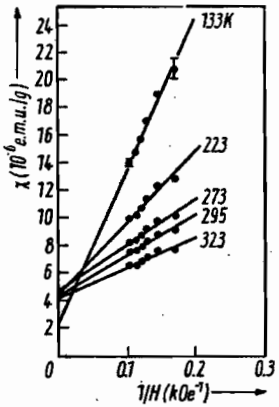

Fig. 2

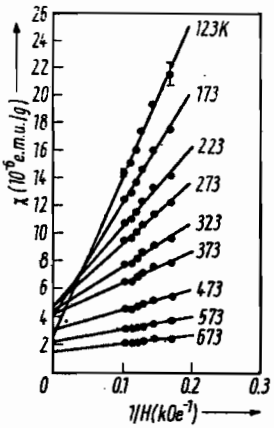

Fig. 3

Fig. 2. Magnetic susceptibility versus 1/H for the hydrated sample

Fig. 3. Magnetic susceptibility versus 1/H for the dehydrated sample

Faraday method. The applied field ranged from 0 to 8 kGs. The obtained results are shown in Fig. 2, 3, and 4. The slope of the total magnetic susceptibility curve versus 1/H (Fig. 2 and 3) gives the ferrimagnetic contribution to the measured susceptibility. This contribution increases with decreasing temperature, and its value is typical for the assembly of superparamagnetic particles. However, at a given temperature this contribution is slightly higher for the dehydrated sample. This might be due to the increase of the superparamagnetic particle sizes during the dehydration process at the temperature of 623 K, and would explain the Zeeman splitting at 78 K observed for the dehydrated sample.

The plots of the total measured magnetic susceptibility values versus 1/H were extrapolated to infinite fields to obtain the paramagnetic plus diamagnetic contributions at a given temperature. The values of these contributions for the hydrated and dehydrated samples as a function of reciprocal temperature are shown in Fig. 4. The curves in Fig. 4 do not obey the Curie rule and their shapes are typical for the assembly of superparamagnetic particles /13/.

From the presented results the following conclusions can be derived. The Mössbauer effect and magnetic susceptibility measurements indicate the existence of an

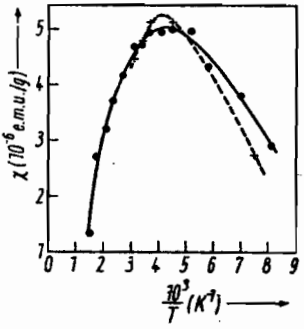

Fig. 4. Paramagnetic plus diamagnetic contributions to the magnetic susceptibility for the hydrated (dashed line) and dehydrated (solid line) samples

assembly of superparamagnetic α-Fe_2O_3 particles with average diameter less than 100 Å in the iron-doped sodium A-type zeolite. Iron ions were not introduced into the Al/Si positions in the zeolite crystal lattice by the method of zeolite preparation mentioned above.

References

/1/ V.I. GOLDANSKII, I.P. SUZDALEV, A.S. PLAZHINDA, and L.G. SHTYRKOV, Dokl. Akad. Nauk USSR 169, 872 (1966).

/2/ W.N. DELGASS, R.L. GARTEN, and M. BOUDART, J. chem. Phys. 50, 4603 (1969).

/3/ W.N. DELGASS, R.L. GARTEN, and M. BOUDART, J. phys. Chem. 73, 2979 (1969).

/4/ J. MORICE and L.V.C. REES, Trans. Faraday Soc. 64, 1388 (1968).

/5/ B.L. DICKSON and L.V.C. REES, J.C.S. Faraday I 70, 2038 (1974).

/6/ B.L. DICKSON and L.V.C. REES, J.C.S. Faraday I 70, 2051 (1974).

/7/ B.L. DICKSON and L.V.C. REES, J.C.S. Faraday I 70, 2060 (1974).

/8/ E.G. DEROUANE, M. MESTDAGH, and L. VIELVOYE, J. Catalysis 33, 169 (1974).

/9/ B.D. MCNICOL and G.T. POTT, J. Catalysis 25, 223 (1972).

/10/ F. SCHMIDT, W. GUNSSER, and A. KNAPPWOST, Z. Naturf. 30a, 1627 (1975).

/11/ J.J. BARA, A. GUTSZE, A.T. PĘDZIWIATR, and Z.M. STADNIK, Proc. Internat. Conf. Mössbauer Spectroscopy, Cracow 1975, Vol. 1 (paper 3B-11).

/12/ W. KÜNDIG, H. BÖMMEL, G. CONSTABARIS, and R.H. LINDQUIST, Phys. Rev. 142, 327 (1966).

/13/ C.J. LIN, J. appl. Phys., Suppl. 32, 233S (1961).

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