MÖSSBAUER EFFECT OF Fe^0-ATOMS IN CATION-EXCHANGED ZEOLITE (TYPE A4)

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The Fe^{2+}-doublet, and the Fe^{3+}-line arising from Auger-electron emission were observed. Electric field gradient, *f*-factor and Debye-temperature were calculated. The dehydrated zeolite shows an additional line whose isomer shift indicates Fe^0-atoms in $3d^8$-configuration.

Measurements on the hydrated and dehydrated synthetic zeolite type A4, $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot \cdot 27\,H_2O$ were carried out at room temperature and 80° centigrade. The dehydration (at a temperature of 150°C and at 0.5 torr) left only 2% of the water in the sample. The Na-ions located almost centrally in a circle of O-atoms with a free inner diameter of 2.6Å, can be exchanged for other single and double valent cations [1]. The Mössbauer source was zeolite-powder saturated with a $^{57}CoCl_2$-solution. A stainless steel absorber was moved with constant acceleration.

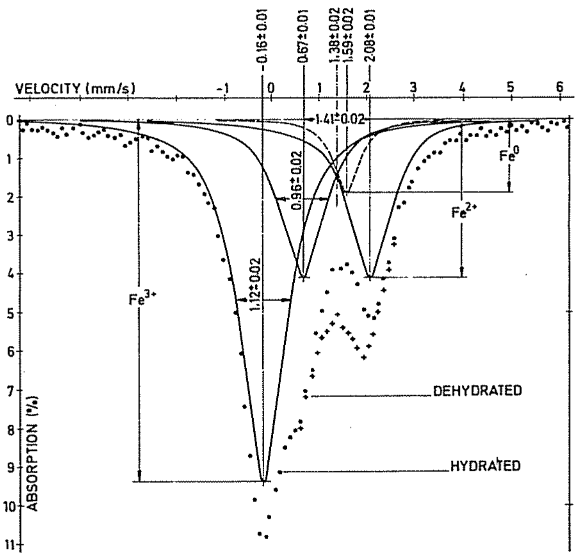

Fig. 1. Mössbauer spectrums of the hydrated and dehydrated zeolite.

The Mössbauer spectra already corrected for radioactive decay and self-absorption are shown in fig. 1. The Fe^{2+}-doublet shows an isomer shift of $v_{is} = +1.38 \pm 0.02$ mm/s and a quadrupole splitting of $v_{qs} = 1.41 \pm 0.02$ mm/s caused by electrical conditions in the zeolite. Auger electrons are emitted after the K-capture in ^{57}Co, and therefore also the line due to Fe^{3+} ($v_{is} = -0.16 \pm 0.01$ mm/s) can be seen [2]. No Mössbauer effect is observed in the liquid phase and so the difference of the two spectra in fig. 1 results from those atoms which were adsorbed in the zeolite lattice when dehydrated. A single line appears with $v_{is} = +1.59 \pm 0.02$ mm/s (fig. 2). Repeated drying and H_2O-saturation did not cause any diminution of the source activity and the measured velocity spectra remained reproducible.

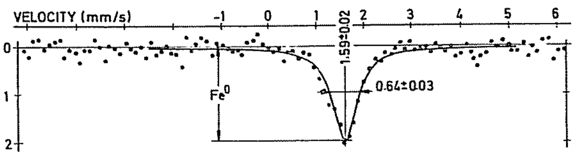

Fig. 2. Difference spectrum (hydrated minus dehydrated) with single peak of the dehydrated zeolite.

An electric field gradient of the sixth 3d-electron with $(7.4 \pm 0.3) \times 10^{17}$ V/cm^2 was calculated from the quadrupole-splitting. A contribution of $(1.1 \pm 0.2) \times 10^{17}$ V/cm^2 was subtracted for the crystal field [3]. This value is derived assuming that the crystal field yields an unresolved splitting of the Fe^{3+}-line which causes the observed greater width of this line, compared to the Fe^{2+}-lines.

The *f*-factor 0.57 ± 0.02 gives a Debye-temperature of 265 ± 10 K for the iron in the zeolite lattice.

The isomer shift is connected with the electron configuration according to Danon [4]. For Fe^{3+}, $v_{is} = -0.16$ mm/s corresponds to a configuration $3d^5 4s^{0.75}$. The s-electron number of 0.75 is presumably due to the covalent part of the Fe^{3+}-binding in the lattice. The shift of +1.38 mm/s of the Fe^{2+}-ions leads to the configuration $3d^6 4s^0$ which is completely adequate to an ionic binding in the zeolite lattice.

The isomer shift $v_{is} = +1.59$ mm/s for the single line observed only in the spectrum of the dehydrated zeolite indicates a $3d^8 4s^0$-configuration. Due to the exchange equilibrium in the humid state of the sample, part of the Co-atoms remain in solution and are then adsorbed inside of the zeolite during drying. In a symmetric position within one of the cages of the zeolite structure the neutral $3d^8$-configuration might be energetically favoured. Decaying, these neutral Co-atoms give the observed contribution of Fe^{0} in the Mössbauer spectrum.

An approximation of the spectrum of the dehydrated zeolite without this Fe^o-line by means of a least squares fit would increase the mean relative error of the measured data points from ±0.16% to ±0.29%.

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References

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