

**Investigation of Iron Doped Sodium A-Type Zeolite
with the Mössbauer Effect Method**

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Aluminosilicates, widely known as zeolites or crystalline sieves, are porous materials with open crystalline structures. Oxygen ions are tetrahedrally ordered around silicon and aluminium ions. The silicon and aluminium tetrahedra form a lattice with regular cages which are interconnected through oxygen windows. The silicon tetrahedra are electrically balanced. However, the aluminium tetrahedra require the presence of an alkali metal or alkaline earth cations in order to maintain electrical neutrality of the aluminosilicate lattice. These cations can take up a number of different positions and are generally accessible for exchange with other ions. They are assumed to constitute the adsorption sites for gas and vapour molecules.

Because of their importance in catalysis and adsorption, zeolites have been the subject of numerous investigations performed with different methods, among which the Mössbauer effect has come to play a considerable role.

On the basis of the results of MMR-measurements, a model of adsorbed water on faujasite type zeolites was developed /1/. In order to get some more information on the behaviour of water adsorbed in zeolites, Mössbauer effect studies on iron doped NaA /4A/ type zeolite were performed and the preliminary results are reported here. Iron atoms were introduced to zeolite not by the commonly used ion exchange method but as an impurity during the preparation process /2/. This iron doping process is thought to enable ferric ions to take Al/Si positions in the zeolite crystal lattice. The sodium A-zeolite hydrated, dehydrated, and rehydrated sample containing 2.39 wt % of natural iron was the subject of our Mössbauer effect investigations. Dehydration was performed at 623 K in vacuum for 12 hours in a thin wall quartz cell that allowed about 70 % transmission of the 14.4 keV gamma rays. Rehydration of the sample took place after the quartz cell was opened. The Mössbauer absorption spectra were taken using a $^{57}\text{Co}/\text{Cr}$ source and constant acceleration spectrometer. The data from absorption spectra were analysed by the least square fitting method. Isomer shifts reported here are with respect to sodium nitroprusside.

The spectra for the hydrated sample were taken at 293 K, 78 K, and 4.2 K, whereas the spectra for the dehydrated one were taken at 293 K and 78 K. The rehydrated sample was measured only at 293 K. For a given spectrum the source and the absorber were at the same temperature. Some these spectra are shown in Fig. 1.

The iron ions introduced to zeolite during the preparation process behaved quite differently from those introduced by the ion exchange method /3/. For the hydrated sample a quadrupole doublet /a/ was observed at 293 K which had $\Delta E = 0.71 \pm 0.01$ mm/sec quadrupole splitting and $\delta = +0.58 \pm 0.01$ mm/sec isomer shift. The lines of the quadrupole doublet became broadened at 78 K and a Zeeman splitting /d/ appeared at 4.2 K from which $H_{\text{eff}} = 494 \pm 10$ kOe was calculated. The dehydrated sample gave at 293 K quadrupole doublet /b/ with $\Delta E = 0.98 \pm 0.01$ mm/sec and $\delta = +0.52 \pm 0.01$ mm/sec but at 78 K it showed a Zeeman splitting /a/ with $H_{\text{eff}} = 501 \pm 10$ kOe. The spectrum of the rehydrated

sample contained at 293 K the doublet /c/ with $\Delta E = 0.84 \pm 0.01$ mm/sec and $\delta = +0.53 \pm 0.01$ mm/sec.

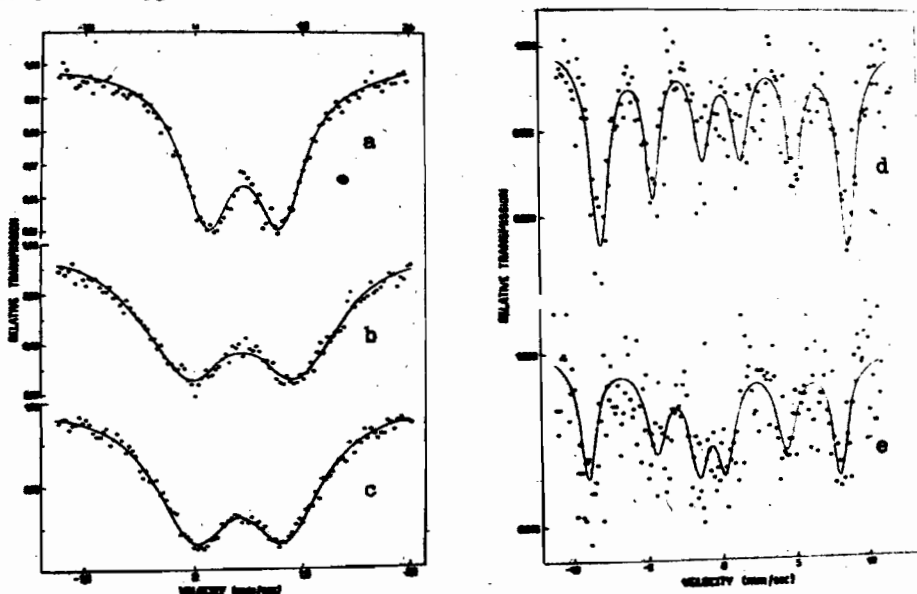


Fig. 1. Spectra of iron doped sodium A-zeolite taken with $^{57}\text{Co}/\text{Cr}$ source for: hydrated sample at 293 K /a/ and 4.2 K /d/, dehydrated sample at 293 K /b/ and 78 K /e/, and for rehydrated sample at 293K /c/.

The quadrupole splitting and the isomer shift were found to be almost temperature independent and practically not influenced by the dehydration process. This, together with the correlation between isomer shift and quadrupole splitting /Duncan diagram/, indicates that there are ferric ions in Al/Si positions of the zeolite crystal lattice. In these positions all ferric ions have a similar coordination and give a simple quadrupole doublet. They are very well screened by oxygen ions and therefore their bondings are almost uninfluenced by adsorbed water molecules. A crystal electric field gradient at ferric ion positions is produced by the charges of sodium ions and is not much dependent on temperature or the state of the dehydration process.

Owing to their polarity and thermal mobility the adsorbed water molecules play a dominant role in spin-lattice relaxation processes. Sample refrigeration and/or dehydration process increase spin-lattice relaxation time. This provides an explanation of the Zeeman spectra /d, e/ observed at 4.2 K for the hydrated, and at 78 K for the dehydrated sample and support the proposed model of adsorbed water /1/.

As was shown in /3/, the ferrous ions, introduced to sodium A-type zeolites by the ion exchange method, are located on or near the walls of the large cavities. They are able to interact with some adsorbed gases, which has a strong influence on Mössbauer absorption spectra.

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References: /1/ H.Pfeifer, A.Gutzze, S.P.Shdanov /to be published in Zeitschr. phys. Chemie /Leipzig/ /. /2/ J.J.Bara, B.Brandt, A.Gutzze, A.T.Łęskiwiatr, Z.M.Stadnik /to be published/. /3/ E.L.Dickson, L.V.C.Rees, J.C.S. Faraday I, 70, 2038 /1974/.