

PREPARATION OF $\text{Fe}^{3+}\text{HNaY}$ ZEOLITES FOLLOWED BY ESR SPECTRA OF THE Fe^{3+} ION

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Preparation of Fe^{3+} zeolites by ion exchange was followed by ESR spectra of the Fe^{3+} ion which make it possible to distinguish between the position of Fe^{3+} in cationic sites of the zeolite structure, in the Si-Al-O skeleton proper and in nondefined Fe^{3+} -O type clusters. In particular, attention has been paid to the pH of aqueous FeCl_3 solutions, where the ion exchange took place. Conditions were determined for the preparation of $\text{Fe}^{3+}\text{HNaY}$ and Fe^{3+}NaY zeolites with isolated Fe^{3+} ions in cationic sites of the zeolite structure.

Zeolite of the faujasite type (Y) in which Na^+ ions are replaced at the same time by H^+ and Me^{n+} ions exhibit a high catalytic activity in carbonogenic reactions of hydrocarbons¹. The Fe^{3+} ion can be one of such active ions; moreover, Fe^{3+} are always present in trace amounts (about 20–2000 ppm) both in synthetic and in natural zeolite forms. Studies concerning the effect of the Fe^{3+} presence (trace or exchanged) on the catalytic activity of the zeolites^{2,3} require both detecting the particular forms of Fe and preparing the zeolites with isolated Fe^{3+} ions in cationic sites of the zeolite structure.

Zeolites containing Fe^{3+} ions have been prepared by ion exchange from aqueous solutions of salts of trivalent iron. However, difficulties exist because of their easy hydrolysis. The hydrolysis results then not only in the formation of isolated Fe^{3+} ions in cationic sites of the zeolite, but also in the formation of clusters of the type Fe^{3+} -O of a non-defined composition which, of course, exhibit different catalytic properties. The exchange cannot be carried out in very acidic solutions, where hydrolysis could be certainly prevented, because a collapse of the crystalline structure of the zeolite could occur. Badran and coworkers⁴ and Morice and coworkers⁵ showed that the zeolites Fe^{3+}NaA and Fe^{3+}NaY can be prepared; they characterized the state of Fe^{3+} by its Moessbauer spectra and the preservation of the crystalline structure by X-ray data. However, they did not pay attention to the possibility of Fe^{3+} -O cluster formation. Derouane and coworkers⁶ were the first to use in their study ESR spectra in order to characterize Fe^{3+} in zeolites. They showed that trace Fe^{3+} occur in cationic sites of the zeolite structure, in the skeleton, where it replace Al, and as occluding salts.

This study shows the possibility of using ESR spectra to follow the formation of various forms of Fe^{3+} during the ion exchange and specifies the conditions for preparing Fe^{3+} in cationic sites of $\text{Fe}^{3+}\text{HNaY}$ and Fe^{3+}NaY type zeolites, in particular with respect to the pH of the solutions used.

EXPERIMENTAL

Zeolites NaY (Linde, Si/Al = 2.4); HNaY-70 (Research Institute of Hydrocarbon Gases, Bratislava, Si/Al = 2.1, 76% of Na⁺ exchanged for NH₄⁺); Fe³⁺HNaY-X and Fe³⁺NaY-X were prepared by ion exchange from NaHY-70 and NaY by exchanging up to X% ions for Fe³⁺ (Table I).

The ion exchange of the initial HNaY-70 and NaY was carried out in aqueous solutions of 0.005 and 0.025 mol/l FeCl₃ at 298 K for 10 minutes. The concentration of hydrogen ions in the FeCl₃ solution was adjusted by NaOH in such a way that the resulting mixture after mixing with the zeolite had pH 4, 6, 10, 14. Besides that, Fe(OH)₃ was prepared separately from the FeCl₃ solution at pH 10 and mechanically mixed with the HNaY-70 zeolite in the ratio corresponding to the Fe content in Fe³⁺HNaY-22. All the zeolite samples were rinsed by distilled water until no reaction on Cl⁻ was observed. Then they were filtered and dried on air. The reverse elution of Fe³⁺ was performed by a multiple rinsing with 0.1M-NaCl.

The analysis of Fe content was carried out, after dissolving the samples, by the absorption spectroscopy method (spectrometer Varian AA 775). The crystallinity of the zeolites was documented by their Ar adsorption capacity at 76 K on the samples dehydrated in the standard way at 520 K at 1.3 · 10⁻³ Pa. ESR spectra of the dehydrated zeolite forms were recorded on an ERS-220 spectrometer (Academy of Sciences of GDR) over the magnetic field range 0–5000 G at λ = 3.2 and 298 K.

RESULTS AND DISCUSSION

ESR spectra of the Fe³⁺ ion make it possible to investigate at least qualitatively the formation of various forms of iron during the ion exchange. The initial HNaY-70 and NaY zeolites contained trace amount of Fe (500 and 350 ppm, respectively) located – according to the ESR spectra (Fig. 1) – in the zeolite skeleton (*g* = 4.3

TABLE I
Characteristics of Fe³⁺ Zeolites

Zeolite	Sorption capacity mmol Ar/g ^a	Amount of Fe ppm	Ionic exchange %
HNaY-70	11.0	350	—
Fe ³⁺ HNaY-3	—	2 500	3
Fe ³⁺ HNaY-5	10.7	4 700	5
Fe ³⁺ HNaY-22	9.4	16 500	22
NaY	9.9	500	—
Fe ³⁺ NaY	10.1	5 200	5

^a Gram of dry zeolite.

$\Delta H = 150$ G) in cationic sites of the zeolite ($g = 2.0$ $\Delta H = 500$ G), and randomly distributed (a broad signal with $g_{\text{max}} = 2.2$ $\Delta H = 1000$ G). The assignment was based on the following results and on the study of Derouane and coworkers⁶. Concerning the ion exchange of Fe^{3+} into cationic sites of the zeolite, one may assume that it would proceed more likely in acidic solutions, while in comparatively alkaline solutions the hydrolysis of Fe^{3+} would take place leading to the formation of $\text{Fe}^{3+}\text{-O}$ clusters of the hydroxidic type. On the other hand, acidic medium carries a danger of a zeolite structure collapse.

For these reasons we investigated during the preparation of the Fe^{3+} zeolites the influence of the solution pH and of the degree of ion exchange on the abundance of various Fe^{3+} forms in the zeolite and on the zeolite crystallinity. It was found (Fig. 1) that during the ion exchange in comparatively acidic solutions (of pH 4 and 6) an increase of the signal $g = 2.0$ ($\Delta H = 500$ G) takes place with the proceeding Fe^{3+} ion exchange. At the same time, the intensity of the fine structure signal (sextet 96 G) increases thus pointing to the presence of Mn^{2+} impurity (up to 30 ppm) in Fe exchanged zeolite. During the reversed ion exchange by an NaCl solution a decrease of the signal intensity at $g = 2.0$ takes place as well as a decrease of the intensity of the fine structure signal. Dehydration of $\text{Fe}^{3+}\text{HNaY}$ and Fe^{3+}NaY zeolites leads to a complete disappearance of the $g = 2.0$ signal. It follows from these

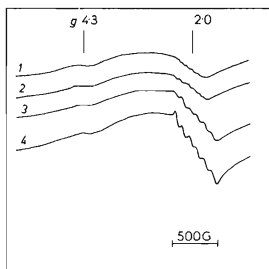


FIG. 1

ESR Spectra of Fe^{3+} in $\text{Fe}^{3+}\text{HNaY}$ Zeolites
 1 Parent HNaY-70, 2 $\text{Fe}^{3+}\text{HNaY-3}$,
 3 $\text{Fe}^{3+}\text{HNaY-5}$, 4 $\text{Fe}^{3+}\text{HNaY-22}$.

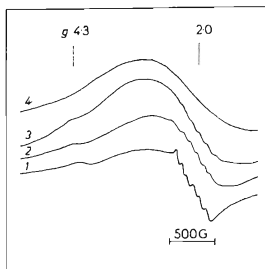


FIG. 2

Dependence of ESR Spectra of Fe^{3+} in $\text{Fe}^{3+}\text{HNaY}$ Zeolites on pH of Ion Exchange Solution (16000 ppm of Fe)

1 pH 4 and 6, 2 pH 10, 3 pH 14, 4 mixture of $\text{Fe}(\text{OH})_3$ and HNaY-70 zeolite.

facts that the $g = 2.0$ signal can be ascribed to the hydrated Fe^{3+} complex in cationic zeolite sites. Further, it turns up that during the ion exchange at pH 4 and 6 no increase of the $g = 4.3$ signal occurs and, therefore, Fe^{3+} does not enter the zeolite skeleton, as expected. Also, the broad signal of $g_{\text{max}} = 2.2$ does not increase under these conditions, but with a larger extent of the ion exchange (22%) its intensity increases. This points to a partial formation of $\text{Fe}^{3+}\text{-O}$ clusters beside the Fe^{3+} in cationic sites.

During the ion exchange in alkalic solutions (pH 10 and 14) with the increasing value of pH a decrease of the $g = 2.0$ signal occurs. The $g = 2.0$ signal corresponds to Fe^{3+} in cationic positions. On the other hand, the increasing intensity of the broad band signal of $g_{\text{max}} = 2.2$ indicates the formation of $\text{Fe}^{3+}\text{-O}$ clusters on the expenses of Fe^{3+} in cationic positions (Fig. 2). When the HNaY-70 zeolite was mechanically mixed with the amount of $\text{Fe}(\text{OH})_3$ corresponding to the Fe content in FeHNaY-22 (pH 4), only a broad a signal in the range 0–5000 G with a maximum at 2.0–2.2 was observed (Fig. 2). This signal reflects the presence of Fe^{3+} particles in the hydroxide and shows that the broad signal of $g_{\text{max}} = 2.2$, observed⁷ in the zeolites, corresponds – in view of its character and the analogy with $\text{Fe}(\text{OH})_3$ – to randomly distributed Fe^{3+} in clusters of the $\text{Fe}^{3+}\text{-O}$ type bound to the zeolite (The intensity values cannot be compared because of different spin-spin interactions.) Analogous results to those following from the ESR spectra of the Fe^{3+} HNaY zeolites were observed also for the Fe^{3+} NaY zeolites.

The reported results show that (a) zeolites Fe^{3+} NaY and Fe^{3+} HNaY with Fe^{3+} in cationic zeolite sites and with preserved crystalline zeolite structure can be prepared, if the ion exchange is carried out in acidic solutions of pH 4 and 6 to the degree of about 20%; (b) ESR spectra of Fe^{3+} ions can be used to obtain information on the form of Fe^{3+} bound in the zeolite, and thus they can be used to monitor the ion exchange into cationic sites of the zeolite.

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