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Studies of the Deammoniation and Dehydroxylation Processes in NH_4 Faujasite and NH_4 Mordenite Zeolites. The Use of the ESR of Framework-Substituted Fe^{3+} as a Probe

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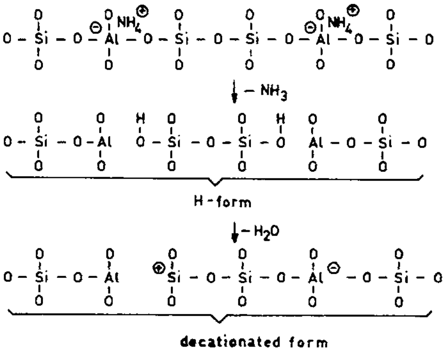
ESR, phosphorescence, and chemical studies of Fe^{3+} impurity in the zeolites faujasite and mordenite have confirmed that the Fe^{3+} species is in the aluminosilicate framework. The appearance of a broad ESR signal upon deammoniation and dehydroxylation of the NH_4 forms of both zeolites in vacuum parallels a decrease in intensity of the normal paramagnetic Fe^{3+} ESR signal. The broad signal is indicative of an Fe/Al oxide species in the zeolite cavities. No such effect was observed in the Na form of mordenite and only a very weak effect was observed in Na faujasite when heated under the same conditions. The products of deammoniation and dehydroxylation of the NH_4 forms of both zeolites had contracted lattices. These effects are interpreted in terms of Kerr's mechanism for Al^{3+} removal from the framework during the formation of ultrastable faujasite.

INTRODUCTION

The nature of the changes which occur in zeolite structures during processes such as deammoniation and dehydroxylation of NH_4 forms has never been clearly defined. This is partly due to the lack of direct studies of the aluminosilicate framework affected by these two processes. Ions such as Al^{3+} and Si^{4+} do not lend themselves readily to direct study by conventional spectroscopic techniques. Most information on the effects of deammoniation and dehydroxylation comes from more indirect techniques such as infrared studies of pyridine adsorption on Brønsted and Lewis acid sites (*1*), and ESR studies of adsorbed organic molecules (*2*) and nitric oxide (*3*).

With the help of these techniques a picture has been built up of the framework changes occurring during removal of ammonia and water; this has been outlined as follows (*4*):



(1)

(2)

On heating the NH_4 form of zeolite Y, for example in a high vacuum or a stream of dry, inert gas to temperatures around 500°C, ammonia is removed, leaving hydroxyl groups on the surface, as evidenced by infrared spectroscopy (*1*). However, if this product is heated between 500 and 700°C the hydroxyl groups are eliminated as water and an unstable product, the decationated form, is obtained. The Lewis acid

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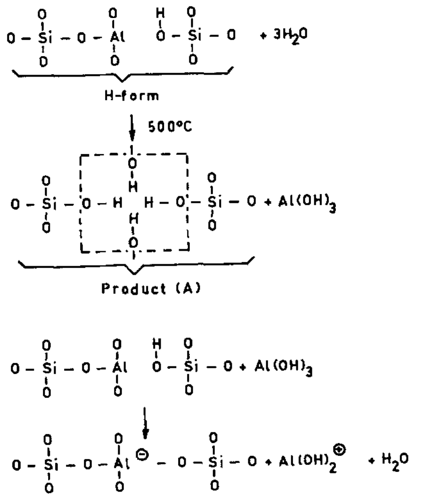
type tri-coordinated Si and Al ions have been identified by pyridine adsorption studies and ESR methods (*1–3*).

Recently, however, McDaniel and Maher (*5*), by special preparative techniques to remove most of the Na^+ ions during exchange with $(NH_4)_2SO_4$, succeeded in obtaining an ultrastable form of decationated zeolite Y. This material was stable to temperatures in excess of 1000°C, whereas normal decationated Y could break down as low as 550°C (*6*). Kerr, using chemical techniques, has since studied this ultrastabilization process in detail (*7*) and has proposed a mechanism whereby under special heating conditions an ultrastable Y zeolite can be obtained. The Kerr scheme can be represented as:



(3)

(4)

This mechanism occurs if the zeolite is heated in a closed or static system after NH_3 removal. The water from the hydroxyl groups can thus remain in the environs to react with the unchanged H-form to give product (A) and $Al(OH)_3$. The ultimate product from reactions (3) and (4) is therefore a faujasite with a higher Si/Al framework ratio and accordingly a higher thermal stability. This product has a lattice constant which is ~1% lower than that of the normal decationated form [reaction (2)]. Kerr has pointed out that the formation of this ultrastable component can occur partially or even completely in vacuum activation if the zeolite bed is deep enough (*7*), i.e., if there is no fast removal of water.

Hence, to solve the question as to which of these processes for deammoniation and dehydroxylation is correct or whether both are correct under specific activation conditions we have attempted to study these effects directly using as tracer the Fe^{3+} which is present as impurity in the zeolites faujasite and mordenite. The first part of this investigation shows that the Fe^{3+} ions were indeed in the aluminosilicate framework—we have published preliminary evidence for this previously (*8*). The second part follows the changes in the environment of the Fe^{3+} ions during deammoniation and dehydroxylation using the ESR of the paramagnetic Fe^{3+} ions as a probe.

EXPERIMENTAL METHODS

a. Materials

Norton Zeolon (synthetic mordenite of chemical composition $Na_2O \cdot Al_2O_3 \cdot 10.9 SiO_2 \cdot 6H_2O$) and Linde SK 40 (Y-type faujasite of chemical composition $0.97Na_2O \cdot Al_2O_3 \cdot 5.04SiO_2 \cdot 9H_2O$) were used as starting materials. Both zeolites contained about 0.1%w Fe. The NH_4^+ forms were prepared by batch exchange at 100°C.

b. Thermal Treatments

Samples of the NH_4 and Na forms of both zeolites were heated in high vacuum for 5 hr at temperatures between 300 and 850°C.

c. Instrumental Techniques

ESR measurements were made on an X-band Varian spectrometer at room temperature and 20 K. Phosphorescence measurements were made on some samples using a Becquerel-type phosphoroscope (*9*). Magnetic susceptibilities were measured using a Faraday balance. The crystallinity of all the samples was checked by X-ray powder diffraction.

RESULTS AND DISCUSSION

a. Evidence for Aluminosilicate Framework Substitution

Previous assertions of isomorphous substitution in zeolites have relied on criteria such as nonexchangeability and chemical analyses; as yet, however, there has been no direct proof of isomorphous substitution. There are a number of possible forms for Fe^{3+} in the zeolites, namely (i) in the aluminosilicate framework with tetrahedral coordination, (ii) in exchangeable sites where the coordination can be fourfold or higher, (iii) as occluded salt molecules, or (iv) as amorphous oxidic material.

We have observed that the Fe^{3+} content in Zeolon and Y zeolites as evidenced by ESR intensities and chemical analyses was not affected by exchange with NH_4Cl solutions: this would imply that Fe^{3+} is not present in accessible ion-exchange sites. The ESR spectra of both hydrated Na^+ and NH_4^+ zeolites were essentially the same, showing intense signals at $g_{eff} = 4.3$ (Fig. 1). This type of signal is well known in the ESR of Fe^{3+} doped polycrystalline solids. It has been observed in glasses (*11*) where the Fe^{3+} ions substitute for Si^{4+} in tetrahedral network forming sites. Griffith (*12*) has shown that this $g_{eff} = 4.3$ signal can arise from either rhombically distorted tetrahedral or octahedral Fe^{3+} species.

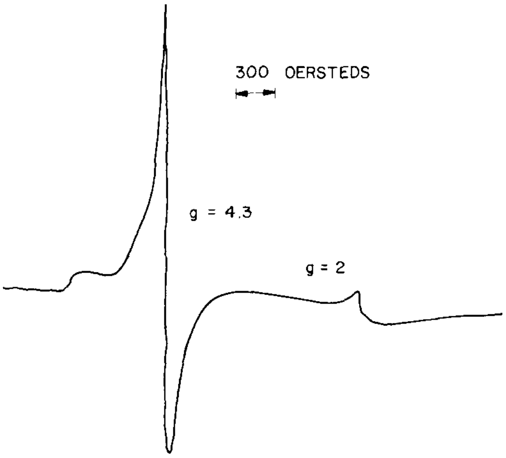


FIG. 1. ESR spectrum of Na Zeolon.

The phosphorescence spectrum of both hydrated Na Zeolon and NaY showed two emissions, one at 480 nm and the other at 680 nm with a weak shoulder at 720 nm. The 480 nm emission, which was excited at 290 nm, is believed to be due to OH radicals in the zeolites generated by UV irradiation (*13*). The phosphorescence red emission and its excitation spectrum are shown in Fig. 2. We have conducted a comprehensive study of the phosphorescence and excitation spectra of Fe^{3+} in oxide and zeolite lattices (*14*) and have established that such a phosphorescence spectrum arises from Fe^{3+} ions in tetrahedral coordination, the transition involved being ${}^4T_1\ (e^3t_2^2) \rightarrow {}^6A_1\ (e^2t_2^3)$. From the excitation spectrum shown in Fig. 2 we have calculated Dq as 640 cm^{-1}. For octahedral Fe^{3+} complexes such as $Fe\ (H_2O)_6^{3+}$ (*15*) and Fe^{3+} in α-Al_2O_3 (*16*) Dq values are at least a factor of two higher.

Apart from the studies described here we have in addition measured the phosphorescence of many other zeolites, e.g., gmelinite, chabazite, phillipsite, erionite, analcime, Linde A, and, in addition, K-feldspars. In all cases we observe emissions between 670 and 730 nm depending on the hydrated state of the zeolite. In all cases the excitation spectra and Dq values were those of tetrahedral Fe^{3+} species.

We can summarize the above observations as follows. The Fe^{3+} species is not in

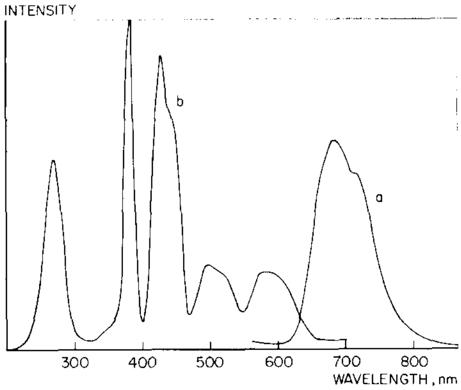


FIG. 2. Phosphorescence (a) and excitation (b) of Fe^{3+} in hydrated Linde Y.

accessible exchangeable sites from the chemical and ESR evidence and from the fact that in the hydrated state the luminescence is characteristic of tetrahedral Fe^{3+}. One would expect that Fe^{3+} ions in accessible exchange sites in hydrated zeolites Y and Zeolon would be at least 6-coordinated. It is unlikely that the Fe^{3+} is present as amorphous occluded oxide since the luminescence is characteristic of a crystalline Fe^{3+} containing compound. The luminescence of Fe^{3+} in amorphous oxides such as SiO_2 and γ-Al_2O_3 gives emissions between 720 and 760 nm *(17)* with charge-transfer band excitation. The possibility of the Fe^{3+} being present as occluded salt molecules can be ruled out because of the identical spectra for all the various zeolite structures and the occurrence of the phosphorescence in feldspars which cannot accommodate salt molecules in their small cages. However, feldspars and zeolites have similar aluminosilicate framework sites. The possibility of the Fe^{3+} ions being in inaccessible cation positions is remote, since there are none in Zeolon; and, in addition, the inaccessible sites in feldspars are not available for Fe^{3+} since these ions are too small and would cause collapse of the aluminosilicate framework *(18)*.

The overwhelming conclusion therefore is that the Fe^{3+} species is present in the aluminosilicate framework of the zeolites and feldspars. This conclusion is further supported by the effect of dehydration and/or deammoniation on the phosphorescence and ESR of Na and NH_4 Zeolon and Y. In NH_4 forms of these zeolites the phosphorescence disappears upon dehydration and deammoniation whereas in the Na forms the signal is undiminished. Since in the decationation process the aluminosilicate framework is disturbed it is understandable that the phosphorescence of Fe^{3+} in the framework should be affected; whereas in the Na^+ forms during dehydration the effect on framework sites would be slight—perhaps a small change in crystal field strength. The ESR results on NH_4 and Na forms of Zeolon during heat treatments also produce different effects, as discussed in the next section.

b. Thermal Studies

The Na form of Zeolon upon heating showed no significant changes in ESR signal (Fig. 3), indicating a negligible effect of dehydration on the coordination of the Fe^{3+} species. The slight increase in intensity in going from hydrated to 400°C heated samples may indicate a small amount of octahedral Fe^{3+} ions in the hydrated zeolite. The NH_4 form of Zeolon, however, above 400°C showed a very broad resonance at $g_{\mathrm{eff}} = 2.3$ (Fig. 4), the intensity growth of which was related to the decrease in intensity of the $g_{\mathrm{eff}} = 4.3$ line; this relationship is shown in Fig. 5. Between 750 and 850°C pretreatments, the broad signal practically disappeared.

The Na form of Linde Y showed no effect on ESR signal up to 500°C pretreatment, but between 500 and 700°C a broad resonance at $g_{\mathrm{eff}} = 2.3$ appeared, more or less similar to that occurring in NH_4 Zeolon, but much less intense. The intensity change of this resonance also followed that of the $g_{\mathrm{eff}} = 4.3$ signal. In NH_4-Y above 400°C, the same broad resonance appeared;

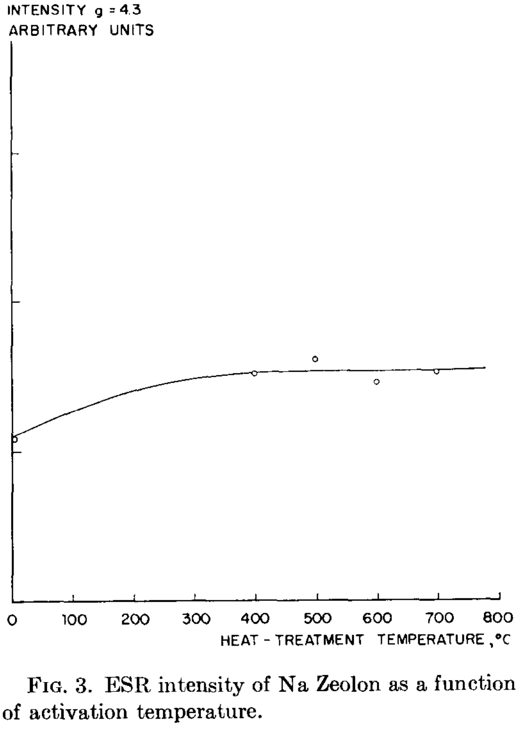


FIG. 3. ESR intensity of Na Zeolon as a function of activation temperature.

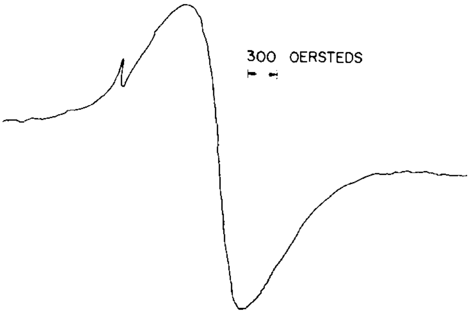


FIG. 4. Broad $g_{eff} = 2.3$ signal observed in $\left\{\begin{matrix}\text{dehydrated}\\ \text{deammoniated}\end{matrix}\right.$ NH_4 zeolites.

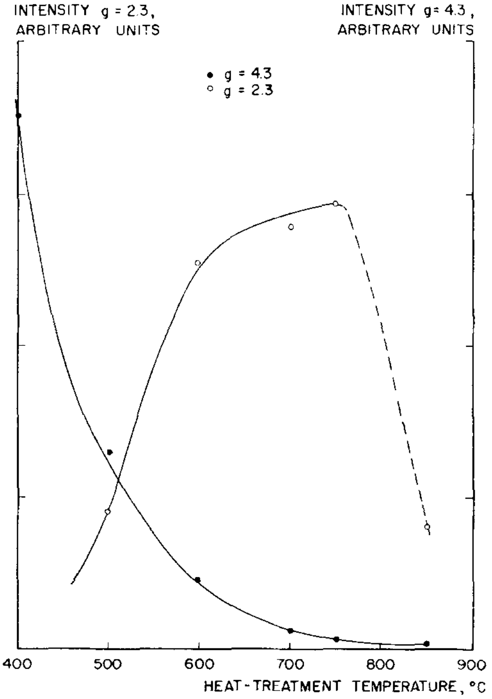


FIG. 5. ESR intensities of NH_4 Zeolon as a function of activation temperature.

but much more intense than in the Na form; and the intensity changes as a function of pretreatment temperature are shown in Fig. 6. Note that here again the intensity changes of this broad signal follow directly the intensity changes of the $g_{eff} = 4.3$ signal. The crystal structure of NH_4-Y deteriorated considerably between 700 and 750°C pretreatment temperatures. The temperature dependence of the broad $g_{eff} = 2.3$ ESR signal, as well as a dependence of the magnetic susceptibility on field strength, are evidence of the presence of cooperative magnetic phenomena, either ferro–antiferromagnetism or superparamagnetism. The most obvious explanation is that during dehydroxylation an iron–oxygen species is precipitating from the lattice.

X-Ray Guinier powder photographs indicated that the lattice of NH_4 Zeolon was somewhat contracted after heating above 700°C. Compared to a sample activated at 500°C this contraction amounted to ~1% in all three directions. Similar contractions were observed in NH_4-Y after heating above 500°C, although the magnitude of

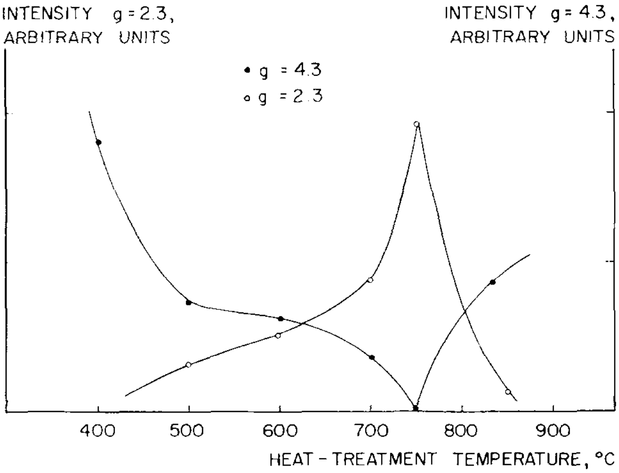


FIG. 6. ESR intensities of NH_4-Y as a function of activation temperature.

the contraction was somewhat greater. Particularly interesting in the case of NH_4-Y was the appearance of double lines in the Guinier photographs of the 500 and 600°C heat-treated forms. For each pair of lines the lattice constant was calculated and the results are shown in Table 1. No contractions were observed in the Na forms of either zeolite.

From the above ESR and X-ray diffraction results, it is apparent that the decationation process in NH_4 Zeolon and NH_4-Y affects both the crystal lattice and the coordination of the Fe^{3+} species; whereas in the case of Na Zeolon heat treatment has no marked effect. In Na-Y only a small effect is observed on the ESR signal.

Broad ESR signals similar to those observed here have been reported previously in NH_4-Y containing Fe^{3+} (*19*) and were described as being ferromagnetic resonance on the basis of magnetic susceptibility measurements. It is obvious that the formation of this resonance is associated with the removal of Fe^{3+} from its framework site: how does this movement of the Fe^{3+} ions arise? The normal decationation process outlined earlier provides only for the formation of tri-coordinated Fe^{3+} ions in the framework, so unless this is a very unstable coordination for Fe^{3+}, it will remain in the framework. The Kerr mechanism, however, provides for a reaction between water derived from hydroxyl groups and lattice Al^{3+} and Fe^{3+} to give $Al(OH)_3$ and $Fe(OH)_3$, which one could readily envisage as forming a compound in the cavities having strong exchange interactions. The drop in intensity of the broad signal between pretreatments of 750 and 850°C may be due to a conversion of this Fe–Al–O species to another form. This is substantiated by a different line shape for the weakened signal.

TABLE 1
LATTICE CONSTANTS OF NH_4-Y

Sample	Pretreatment temp (°C)	Lattice constant (10^{-10} m)
NH_4-Y, 1	500	24.79
2	500	24.32
NH_4-Y, 1	600	24.81
2	600	24.35

It would appear that under the conditions of our experiments the Kerr process for decationation occurs. Our activation cell was narrow in relation to the depth of the zeolite bed, so even although the activation was done under high vacuum the system was no longer dynamic as compared to a system where there is a shallow bed or where the activation is conducted under a stream of inert gas. Thus under our conditions water from dehydroxylation had time to react with framework ions to form an Al-deficient product and an Fe–Al–O species in the zeolite cavities. The small effect observed with NaY is due to the cation deficiency in this zeolite, i.e., there is a small concentration of OH groups on the zeolite framework.

The lack of control of the decationation process in our experiments may explain the deterioration in crystallinity of NH_4-Y and to a lesser extent of NH_4 Zeolon after heating above 700°C, i.e., too much Al^{3+} is removed from the framework under our conditions. As a result, we have simulated the experimental conditions of Kerr's process for decationation and applied them to NH_4 Zeolon. A highly crystalline product was obtained, which showed a uniform lattice contraction of 1%. Another sample of NH_4 Zeolon was heated at the same temperature (700°C) as the "Kerr process" sample, but in a stream of dry nitrogen. A highly crystalline product was again obtained; however, no detectable lattice contraction was observed in this case. These results are summarized in Table 2.

An interesting point to be noted for these two samples was the ESR results. The sample treated in dry N_2 showed a broad signal similar to that of the samples mentioned earlier in this discussion. This fact, allied to the result that the lattice did not contract, indicates that in this sample *only* Fe ions precipitate from the framework (or Fe ions plus an insignificant number of Al ions). This might reflect the instability of Fe^{3+} in tri-coordination or, more likely, incipient lattice destruction: the normal de-

TABLE 2

LATTICE CONSTANTS OF NH_4-ZEOLON

Sample	Pretreatment temp (°C)	Lattice constant (10^{-10} m)
Na Zeolon	—	$a = 18.13$
		$b = 20.48$
		$c = 7.52$
NH_4 Zeolon	700 in dry N_2	$a = 18.13$
		$b = 20.40$
		$c = 7.49$
NH_4 Zeolon	450 *in vacuo* then 700 in closed system	$a = 17.94$
		$b = 20.18$
		$c = 7.41$

hydroxylated forms of zeolites are very unstable.

In the sample heated under conditions for the formation of pure ultrastable mordenite the ESR showed only a very weak broad background together with the characteristic $g_{eff} = 4.3$ signal (somewhat weakened compared with Na Zeolon treated similarly) and another paramagnetic signal at $g_{eff} = 2.0$ of width 30 G. This second signal at $g_{eff} = 2.0$ may be due to Fe^{3+} ions in sites other than aluminosilicate framework sites. It is well known that the mechanism for formation of ultrastable zeolites converts framework Al^{3+} into exchangeable $Al(OH)^{2+}$, $Al(OH)_2^{+}$ species. Presumably hydroxylated Fe^{3+} and Al^{3+} cations are created on formation of ultrastable mordenite. The paramagnetic signal at $g_{eff} = 2.0$ could perhaps be due to cationic hydroxylated Fe^{3+} species, since its appearance was accompanied by a decrease in the $g_{eff} = 4.3$ framework Fe^{3+} signal.

CONCLUSIONS

From the observations reported here it is apparent that the aluminosilicate framework of zeolites can be substituted by paramagnetic transition metal ions of suitable size and valency such as Fe^{3+}. The spectroscopic properties of such ions can be used as probes for changes occurring in the framework during processes such as dehydroxylation and deammoniation.

The mechanism proposed by Kerr for the removal of Al^{3+} from the framework during the formation of ultrastable zeolites has been substantiated by our result.

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