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ESR Study of Deep-Bed Calcined NH_4Y and Aluminum Deficient Zeolites

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Electron spin resonance and irradiation by γ-rays at 77°K or at room temperature were used to study the removal of alumina from the Y type zeolite framework by heat treatment in a deep bed geometry.

X and *Q* band ESR spectra were recorded at 77°K and showed respectively 12 and 16 lines corresponding to an isotropic hyperfine interaction with two aluminum atoms ($I = 5/2$) ($c_\parallel \simeq c_\perp \simeq a^{Al}_{iso} = 10.0$ Oe), the eleven hyperfine lines being split by a uniaxial symmetry of the g tensor ($g_\parallel = 2.0125$, $g_\perp = 2.0030$, and $g_{iso} = 2.0062$). The paramagnetic center was identified with a *V* center, namely a hole of an electron trapped on an oxygen atom bonding two nearby aluminum atoms. This center is localized on alumina which has been removed from the zeolite framework. The removal of alumina occurred only when the samples were heated above 400°C in the presence of both water vapor and ammonia. It is suggested that the mechanism of migration involves the formation of aluminic acid in a dimer form and a reorganization of the lattice leaving no aluminum atom vacancies. A special emphasis is placed on the heat treatment conditions.

INTRODUCTION

Particular attention has been paid quite recently to the so-called ultrastable zeolites which can be prepared by heat treatment in an ammonium sulfate solution (*1*), or by removal of alumina from the lattice either by chemical extraction in solution (*2*, *3*) or by heating in a deep-bed geometry (*4*, *5*). In the latter procedure, it is commonly assumed that a migration of alumina occurs during the thermal decomposition of NH_4Y zeolite in the presence of water vapor and in a geometry which impedes the removal of amomnia from the bed. The migrated alumina is quite easily dissolved in 0.1 N NaOH solution.

Using ESR spectroscopy and irradiation by γ-rays at room temperature, we have studied the mechanism of ultrastabilisation by transfer of alumina in H-Y type zeolite.

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EXPERIMENTAL

Different kinds of samples, heat treated under different conditions, were prepared in the following manner starting from a Na-Y zeolite supplied by Linde Co.

(i) In a conventional exchange procedure using a 0.1 M solution of NH_4NO_3, a NH_4Y sample was obtained with 90 percent Na^+ ions exchanged by NH_4^+ ions. The heat treatment procedure which followed is one which is conventionally used in our laboratory. The samples, placed with a 20 mm ht of powder in a 4 mm i.d. ESR tube sealed on an ungreased vacuum line, were heated at 600°C for 16 hr in 160 Torr oxygen pressure, in order to avoid pollution by hydrocarbons. This partial O_2 pressure was obtained by filling the vacuum line with air and cooling the trap to liquid nitrogen temperature. This procedure is similar to the deep-bed (DB) geometry treatment described by Kerr (*4*). Our samples were then

evacuated under vacuum ($<10^{-5}$ Torr) for 20 hr and denoted Y-DB.

(ii) In order to specify the influence of this procedure on our results, some samples were prepared in such a way as to remove gases during the heat treatment. The samples were carefully outgassed before and during the heat treatment up to 600°C in a shallow-bed (SB) geometry. They were then oxidized at 600°C by air as reported above and re-evacuated at 600°C. They will be denoted Y-SB.

(iii) Aluminum deficient samples, denoted AlD, were prepared starting from NaY or $NaNH_4Y$ zeolite with varying Na content by chemical extraction using either acetylacetone (AA) in CCl_4 solution or ethylenediaminetetraacetic acid (EDTA) in water, according to the methods of Beaumont and Barthomeuf (*2*) and Kerr (*3*). The compositions of the samples are listed in Table 1.

The ESR spectra were recorded at 77°K with a Varian (V 4502) spectrometer using the 9.4 (*X* band) and 35 GHz (*Q* band) microwave frequencies. In *X* band, a dual cavity was used and the *g* values were measured by comparison with a DPPH sample ($g = 2.0036$). In *Q* band they were determined from the H atom doublet lines observed for a 77°K γ-irradiated zeolite [$g_{iso} = 2.00246$ (*6*)] after a second order correction which takes into account the downfield shift of the center of the doublet equal to $a^2/4\ H_0$ in field units with $a^H_{iso} = 501.8$ Oe for H atoms.

In special experiments, aliquots of the DB and AlD-DB samples were extracted with 0.1 N NaOH (*3*). The filtrates were chemically analysed to determine if alumina and silica had been removed from the lattice and dissolved. Some samples were then washed with distilled water, dried, and heat treated according to the standard procedure.

Irradiations were performed in a γ-ray Co^{60} cell built in the laboratory at room and liquid nitrogen temperatures for about a 4 Mrad dose.

Results

γ-Irradiation at 77°K of all samples heat treated at 600°C gives rise to an ESR spectrum composed of a circa 500 Oe hf splitting doublet due to H atoms (*6*) and a broad (40–60 Oe wide) and complex signal centered at $g \simeq 2.01$, due to the superposition of several component signals (Fig. 1a).

Looking for the latter signal as a function of the heat treatment conditions described above we noticed the following.

(*a*) For Y-DB samples irradiated at 77°K, it seems that one of the component signals involves many hyperfine lines. Indeed, when the samples are warmed up to room temperature, the overall signal amplitude decreases, and a 12 hyperfine line signal emerges from the complex signal (Fig. 1a and b).

(*b*) For Y-SB samples irradiated at 77°K, the 12 line hyperfine signal does not show up, even after warming up to room temperature. Only a complex signal is observed (*23*).

(*c*) AlD samples which had undergone a DB treatment (procedure i) gave at 77°K a signal quite similar to the signal obtained in Case *a*. However, when the samples are warmed up to room temperature or irradiated at this temperature, the nearly pure 12-line spectrum is observed as shown in Figs. 2 and 3.

If the AlD samples undergo a SB treatment (procedure ii), the 12-line signal is not obtained.

TABLE 1

Anhydrous Unit Cell Composition of the Different Samples before the Heat Treatment

	Samples	Formula
1	$NaNH_4$	$Na_5(NH_4)_{51}(AlO_2)_{56}(SiO_2)_{136}$
2	AlD-NH_4^+, I, AA	$Na_{29.6}(NH_4)_{8.5}(AlO_2)_{38.1}(SiO_2)_{136}$
3	AlD-H^+, II, AA	$Na_{40}H_{7.6}(AlO_2)_{47.6}(SiO_2)_{136}$
4	AlD-NH_4^+, EDTA	$Na_{3.1}(NH_4)_{27.4}(AlO_2)_{30.5}(SiO_2)_{136}$

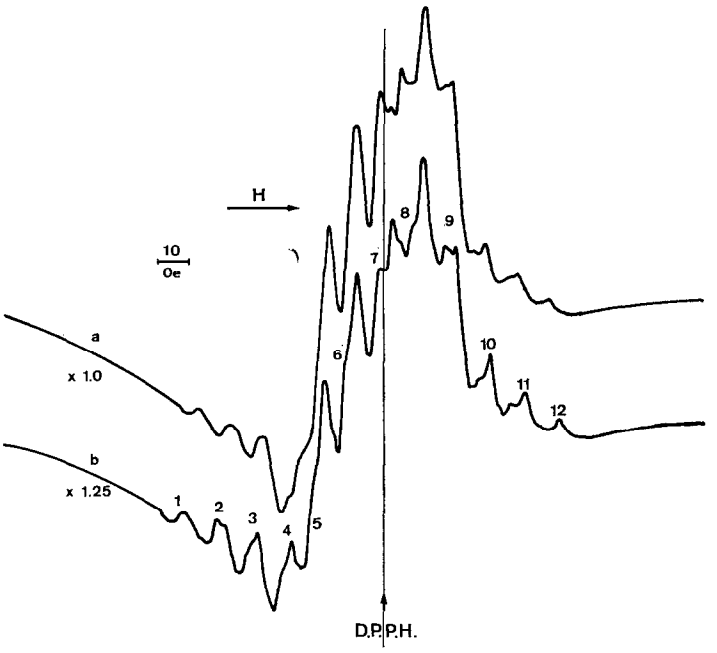


FIG. 1. 77°K X band spectra of a deep bed $Na_5(NH_4)_{31}(AlO_2)_{56}(SiO_2)_{136}$ zeolite heat-treated at 600°C and γ-irradiated at 77°K. (a) After irradiation, (b) after warming up to room temperature for 20 min.

The DB treatment is known to form ultrastable zeolite (*4*). As the 12-line signal is only observable in DB conditions, we think that this signal is in some way connected with the ultrastabilisation of the zeolite.

The X and Q band spectra recorded at 77°K after irradiation of sample 2 at room

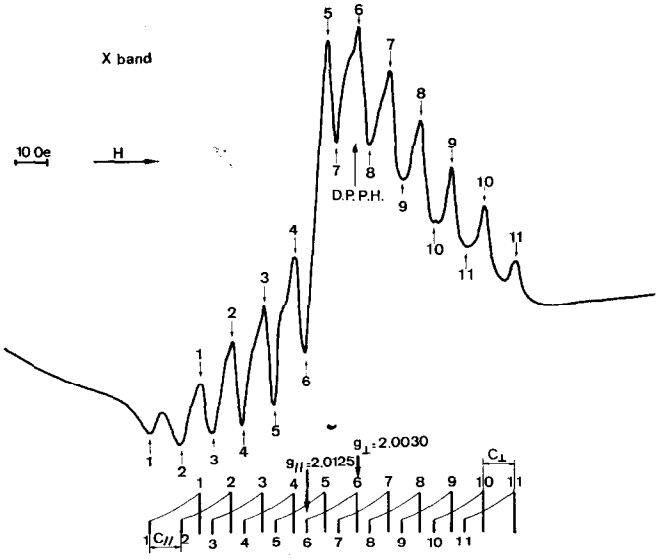


FIG. 2. 77°K X band spectrum of a deep bed $Na_{29.6}(NH_4)_{8.5}(AlO_2)_{38.1}(SiO_2)_{136}$ zeolite heat-treated at 600°C and γ-irradiated at 300°K.

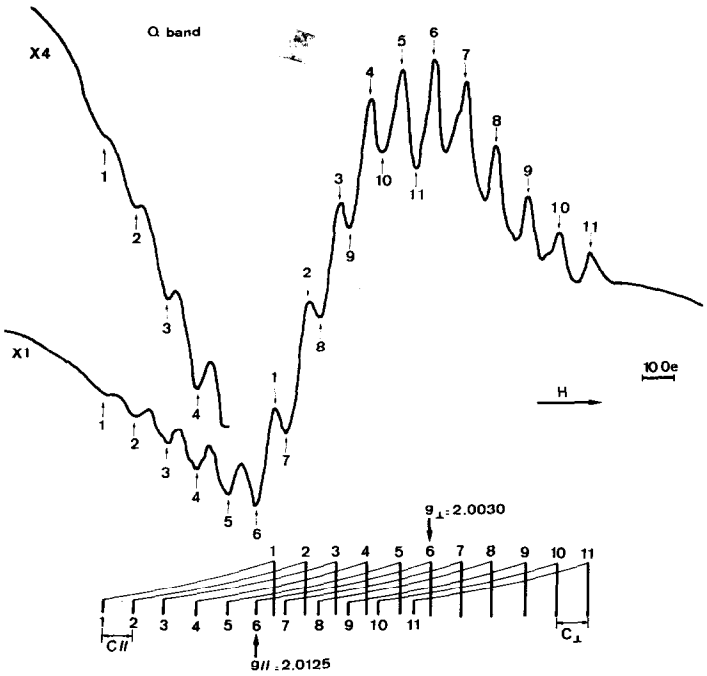


FIG. 3. 77°K Q band spectrum of a deep bed $Na_{29.6}(NH_4)_{8.5}(AlO_2)_{38.1}(SiO_2)_{136}$ zeolite heat-treated at 600°C and γ-irradiated at 300°K.

temperature are given and analyzed in Figs. 2 and 3. The corresponding 12- and 16-lines can be attributed to an eleven hyperfine structure split by a uniaxial g anisotropy as indicated in the corresponding stick spectra shown in the figures. The ESR parameters are $g_\parallel = 2.0125$, $g_\perp = 2.0030$, and $g_{iso} = 2.0062$; and $c_\parallel \simeq c_\perp \simeq a_{iso} = 10.0$ Oe.

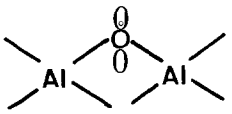
It was difficult to compare the intensities of the 12-line spectra for the different samples because of the overlapping of the complex, 40 Oe wide, spectrum. Nevertheless, the number of paramagnetic centers is of the same order of magnitude and roughly equal to 5×10^{19} centers per gram for the 4 samples.

Nature of the Paramagnetic Center

The eleven line hyperfine structure is due to the coupling of the unpaired electron with two equivalent aluminum atoms ($I = 5/2$). The ESR signal is not saturated when increasing the microwave power and its g-values are larger than g_e (2.0023). Hence, we can argue that the paramagnetic center is a trapped hole (*7*) produced by irradiation.

It is noteworthy that one has $g_x \simeq g_y = g_\perp \neq g_\parallel$ indicating a uniaxial symmetry, in contrast with $c_x \simeq c_y \simeq c_z \simeq a_{iso}$. For a uniaxial symmetry, the principal values of the hyperfine $\hat{c}$ tensor are given by $c = a + b\ (3\cos^2\theta - 1)$. The isotropic constant a equals $A_0\ C_{3s}^2$ with $A_0 = 981$ Oe (*8*), the anisotropic constant b equals $B_0\ C_{3p}^2$ with $B_0 = 21$ Oe (*8*) and θ is the angle between the aluminum $3p$ axis and the static magnetic field. C_{3s}^2 and C_{3p}^2 are the spin densities of the unpaired electron on the $3s$ and $3p$ orbitals of the aluminum atom. The total, isotropic plus anisotropic, hyperfine splittings are: $c_\parallel = a + 2b$, $c_\perp = a - b$, and $|c_\parallel - c_\perp| = 3|b|$. Taking into account the inaccuracy in measuring the $c_\parallel$ and mainly the $c_\perp$ splittings from a powder shape spectrum [the parallel and perpendicular c values are taken at the turning points of the ESR spectrum according to Lebedev (*9*)], one has $3|b| \leqslant 0.6$ Oe. Since $a_{iso} = 10.0$ Oe and $|b| \leqslant 0.2$ Oe, the spin density is about 1% in the $3s$ orbital of the aluminum atom and less than 1% in its $3p$ orbitals. The unpaired electron is equally coupled to two aluminum atoms and the

electron spends less than 4% of its time on the aluminum atoms and 96% on atoms with nuclear spin equal to zero. Since the aluminum atoms are bonded to an oxygen atom with $I = 0$, the unpaired electron is presumably essentially localized on the oxygen atom. Taking into account that the electron is equally coupled with two aluminum atoms, we suggest that the V center we are dealing with is a hole of an electron localized in a non-bonding sp^2 orbital of the oxygen bridging two aluminum atoms, as represented below.



This model implies that during the DB heat treatment, a migration of Al from the zeolite framework occurs. The ESR spectrum may characterize this migration. Moreover, it is very important to emphasize that we have never observed such a well-resolved ESR spectrum in any kind of stoichiometric alumina. For instance, in α-Al_2O_3, γ-Al_2O_3, boehmite, gibbsite, and bayerite we have obtained broad (about 40 Oe wide) and unresolved signals with $g_{app} \simeq 2.010$. In other words the V center we are interested in belongs to a quite peculiar alumina.

The model we propose can be likened to an O^- ion in a crystal field with axial symmetry, but in that case $g_\perp > g_e$ and $g_\parallel \simeq g_e$ is to be expected (*10*), in disagreement with experiment. However, for a M–O^- type of center in alkali glasses, $g_\parallel > g_e$ and $g_\perp \simeq g_e$ are observed. This situation is explained by a change of the relative ordering of the energy levels in the molecular orbitals of M–O^- compared to those of O^- (*11*) and this point supports our interpretation.

An eleven hyperfine structure has been reported for HY and AlHY zeolites (*12*) γ-irradiated under vacuum ($a_{iso} = 10.0$ Oe and $g_{iso} = 2.007$). However, it seems to be composed of 12 hyperfine lines and quite similar to ours.

It is important to recall that when the samples undergo a SB treatment (procedure ii), the complex, 40 Oe wide, signal is obtained but never the 12-line spectrum. Thus, we argue that the 12-line spectrum is connected with the migration of alumina occurring during the DB treatment.

In some particular DB experiments on sample 1, we obtained the spectrum given in Fig. 4. This spectrum is mainly composed of a sextet (six lines of about equal intensity) with $g_{iso} = 2.0048$ and $a_{iso}^{Al} = 9.5$ Oe, superimposed on a small 12-line spectrum. This sextet can be attributed to a hole of

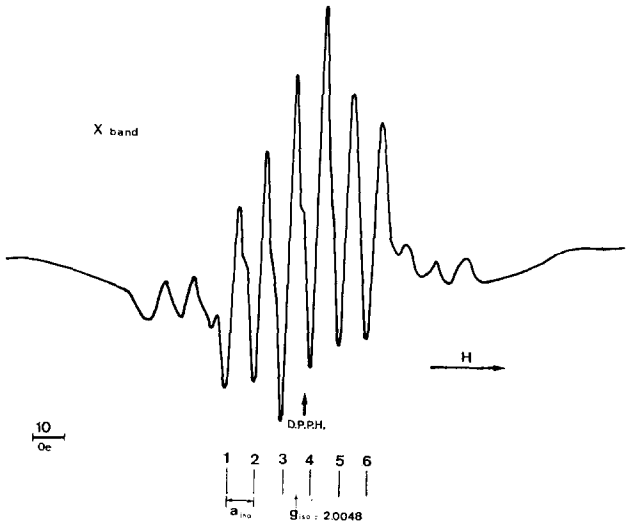


FIG. 4. 77°K X band spectrum of a DB $Na_5(NH_4)_{51}(AlO_2)_{56}(SiO_2)_{136}$ zeolite irradiated at 300°K under vacuum.

an electron localized on an oxygen atom which is bonded to only one aluminum atom ($I = 5/2$). Its g_{iso} and a_{iso} values are close to those observed for the 12-line spectrum. Consequently, we are of the opinion that the 12-line spectrum corresponds to a dimer of an aluminated species, which gives rise to an isotropic six-line spectrum in a monomer form.

Reactivity of the Paramagnetic Center

The V center we are dealing with was found to be very reactive with oxygen even at 77°K. On sample 2, which gives the purest 12-line spectrum, an oxygen species stable at temperatures up to 250°C has been observed. Its ESR parameters are $g_z = 2.0575$, $g_y = 2.0085$, and $g_x = 2.0026$ (Fig. 5). This species is presumably an O_2^- species. The g_z component value is much higher than expected for O_2^- adsorbed on a trivalent Al [$g_z \simeq 2.034$ (*13*)] or a tetravalent Si atom [$g_z = 2.024$ (*14*)], which may be due to a partially covalent bond between O_2 and Al or Si, as pointed out by Känzig *et al.* (*15*), or to adsorption on a divalent ion (*16*). When irradiation is carried out in the presence of 20 Torr of oxygen, two oxygen species are obtained. One has about the same ESR parameters as above and can be attributed to the same O_2^- ion. It is stable up to 250°C. The other one, stable up to 50°C, has different g-values: $g_z = 2.0142$, $g_y \simeq 2.008$, and $g_x \simeq 2.002$ (Fig. 5). In view of its g-values, the latter species can be attributed to an O_3^- ion (*17*) formed by adsorption of oxygen on an O^- ion created by irradiation.

No superhyperfine interaction of the unpaired electron of the oxygen species with aluminum atoms has been detected. This result can tentatively be interpreted as a proof of the adsorption of oxygen on an atom with a nuclear spin equal to zero, what is quite in agreement with the model we have suggested for the V center ($I = 0$ for O atoms).

Conditions of Paramagnetic Center Formation

It was shown above that the paramagnetic center corresponding to the 12-line spectrum is connected with a peculiar alumina which originates from the migration of aluminum atoms under DB treatment. It turned out that the ESR technique permits us to follow this migration.

In order to specify the determining fac-

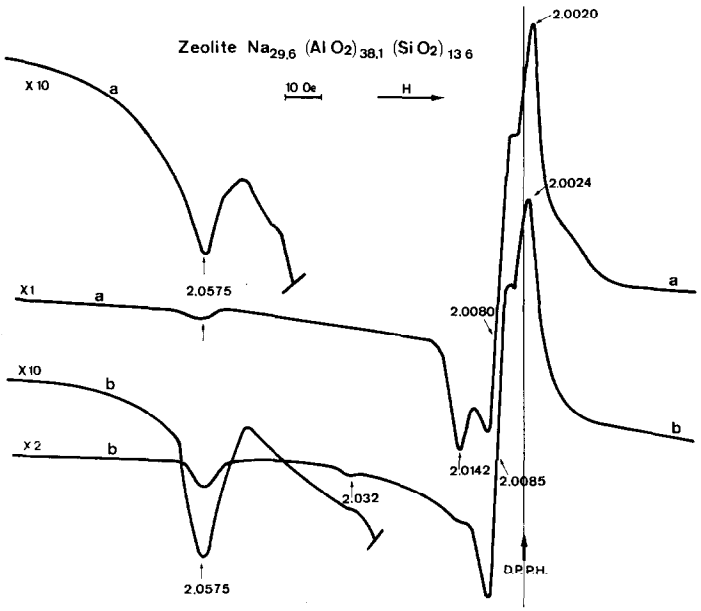


FIG. 5. 77°K X band spectra of a DB $Na_{29.6}(NH_4)_{8.5}(AlO_2)_{38.1}(SiO_2)_{136}$ zeolite irradiated at 300°K in the presence of 20 Torr of oxygen. (a) Initial spectrum, (b) after warming at 150°C for 6 hr.

tor in this migration, samples were heat treated in controlled atmospheres. In these experiments, the zeolites were first outgassed at 400°C, in order to remove ammonia and water, and then oxidized at the same temperature. Compounds which may play a role are water, ammonia, and oxygen. Consequently, a given gas or vapor (dry oxygen, water, dry ammonia, or water plus ammonia) was adsorbed overnight at room temperature on the 400°C pretreated samples. We then observed that only the $H_2O + NH_3$ atmosphere produced the 12-line spectrum. It is also important to note that the NaY sample did not give a 12-line spectrum even in DB geometry, this being attributable to the absence of ammonia.

In order to demonstrate that the 12-line spectrum is only observed when migration of alumina occurs, we have extracted this migrated alumina by a 0.1 N NaOH solution according to the method of Kerr (*4*). In all previous experiments, we found alumina but no silica by chemical analysis of the NaOH filtrate, only when the samples underwent a DB or $H_2O + NH_3$ atmosphere treatment. When this alumina was dissolved, we have dried and heat-treated the samples according to procedure ii (SB). After irradiation no 12-line spectrum and no dissolution of alumina were observed.

These results show that the 12-line spectrum is connected with the migrated alumina and not with the ultrastabilized framework. However, one can also argue that the NaOH treatment may reorganize the aluminum deficient lattice with disappearance of the Al-O-Al species. Nevertheless, we have observed that the number of *V* centers varies as the amount of migrated alumina chemically determined in the NaOH filtrate. We have indicated above that the number of paramagnetic centers is roughly equal to 5×10^{19} g^{-1}, corresponding to 10^{20} migrated aluminum atoms. In the DB treatment (sample 1), the number of migrated aluminum atoms given by Kerr (*4*) equals 10.4 per unit cell, namely 5×10^{20} g^{-1}, which is in fairly good agreement with the ESR data.

At this point it seems interesting to compare the behavior of two kinds of aluminum-deficient zeolites undergoing the same DB treatment. The first sample is a Y-DB zeolite for which migrated alumina [10.4 Al/unit cell (*4*)] has been dissolved in NaOH solution. The second one is an AlD sample (sample 2) from which 18 aluminum atoms have been chemically extracted. After a DB treatment only a small 12-line spectrum was obtained for the first sample, whereas the second one gave rise to an intense spectrum (e.g., see Fig. 2). It may consequently be concluded that the alumina removal by chemical action still leaves Al ions sensitive to the action of steam and ammonia.

Discussion

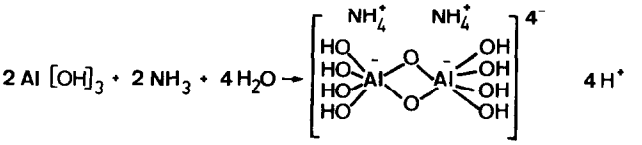
The paramagnetic *V* center with which we are concerned has been found to be strongly dependent on the nature of the heat treatment. It has only been obtained for samples heated in drastic conditions allowing the alumina to be removed from the lattice. This center is connected with a quite peculiar aluminated species which originates from the zeolite framework.

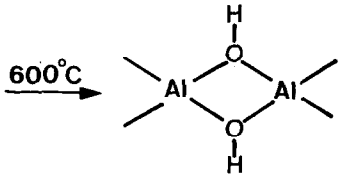
Kerr (*4*) has shown that cationic aluminum is present in a zeolite which has undergone the standard DB treatment and he has suggested a mechanism of formation of aluminum hydroxide and then $Al(OH)_2^+$ cation. Kerr's postulation of the formation of $Al(OH)_3$ as part of the mechanism for aluminum removal agrees with our ESR findings. However, in view of the hyperfine splitting constant which we observed, we feel that the mechanism for aluminum removal may be somewhat different from that given by Kerr. An $Al(OH)_2^+$ cation ionized by γ-rays should give rise to a large hyperfine splitting of the unpaired electron, essentially localized on the aluminum atom. As a matter of fact, Hervé (*18*) observed an Al^{2+} center with the following ESR parameters: $c_{\parallel} = 212.5$ Oe and $c_{\perp} = 179$ Oe, $g_{\parallel} = 2.0004$ and $g_{\perp} = 2.0015$, data which are quite far from our results.

We have reported above that the ESR spectra are observable only when the DB heat treatment is carried out in the presence of both steam and ammonia. The aluminum hydroxide, $Al(OH)_3$, formed according to the first step postulated by Kerr is

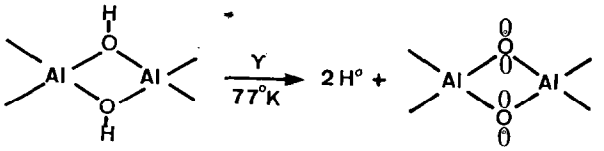
amphoteric. Consequently, it can be argued that over an ammoniated atmosphere the hydroxide is transformed into an ammonium aluminate which is decomposed at the elevated temperature of treatment into aluminic acid. Such an acid is known to be stable as a dimer in liquid phase up to 30°C (*19*).

The mechanism of alumina removal, as we envisage it, is given below:





Under irradiation at 77°K, this acidic compound may lead to the formation of H atoms and *V* centers according to the scheme:

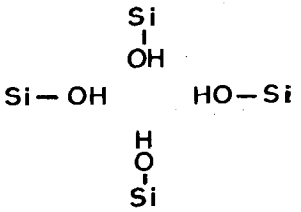


The *V* center corresponds to a dimer with tetracoordinated aluminum atoms. This structure may explain why we never observed such centers in other types of alumina.

We have shown previously (*20*) that irradiation at 77°K of a HY zeolite (NH_4Y sample treated at 400°C according to procedure ii) gives rise to trapping of H atoms whose ESR line width equals 1.25 Oe and which have been related to acidic OH groups. When the samples are treated at 600°C in SB geometry, only a small number of H atoms are trapped and the width of their ESR lines equals about 0.9 Oe. These H atoms have been related to a silica impurity within the solid. However, if the same sample is treated at 600°C in DB geometry (instead of SB) and irradiated at 77°K, 1.25 Oe wide H lines are observed. This seems to show that in these conditions acidic OH groups may be formed. These results are in good agreement with the scheme we have proposed.

In good agreement also with our ESR findings, Maher *et al.* (*21*) reported some X ray data obtained for ultrastable faujasites prepared according to the procedures described by McDaniel and Maher (*1*). They found that of the three hydroxyl groups coordinated to each aluminum ion in $S_{I'}$ sites (migrated aluminum are shown to occupy cationic sites), two are shared with another $S_{I'}$ aluminum ion and the other is not shared. Recall that in these zeolites the migrated alumina has not been eliminated from the sample.

Moreover, in the mechanism of formation of $Al(OH)_3$ given by Kerr (*4*), extraction of alumina leads to the creation of a vacancy of aluminum atoms as shown below.



Such a vacancy may probably be ionized by γ-rays into a paramagnetic *V* center which may presumably present a hyperfine interaction with the surrounding protons. In

fact, we did not observe any change in the shape of the ESR spectra on dealuminated samples compared to conventional HY zeolite after SB and DB treatments, the 12-line spectrum excepted. In this laboratory it has been shown by X ray work (*22*) that the Si, Al occupancy factor in the lattice remains equal to one when dealuminating the samples by chemical treatment. Consequently, ESR and X ray results can be interpreted in terms of migration of certain Si atoms towards the vacancies created by the aluminum atom removal.

Conclusions

Using the ESR technique and γ-irradiation, we have been able to show the importance of the heat-treatment conditions on the properties of the zeolite. Our experiments show that the formation of ultrastable zeolite is strongly dependent on the geometry of the ammonium Y zeolite bed during thermal decomposition.

The aluminum-deficient zeolites prepared by chemical action have been found to have still aluminum ions sensitive to the action of steam and ammonia.

The migration of alumina has been shown to depend upon the presence of both water and ammonia during the heat treatment at 600°C. The proposed mechanism of migration involves the formation of aluminum hydroxide by steam and its attack by ammonia giving rise to a dimer (or sometimes a monomer) of aluminic acid. Formation of $Al(OH)_2^+$ or $Al(OH)^{2+}$ species as well as aluminum vacancies in the framework during dealumination seems unlikely.

Acknowledgments

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