PHYSICAL AND INORGANIC CHEMISTRY

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Electron Spin Resonance of Molecules Adsorbed on Synthetic Zeolites

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RECEIVED SEPTEMBER 3, 1963

The electron spin resonance absorption characteristics were determined for a number of molecules adsorbed on both sodium zeolite of type Y and decationated zeolites prepared from it. Adsorption was also determined spectrophotometrically. Electron charge-transfer complexes were found when molecules with low ionization potential were adsorbed on decationated type Y zeolite. The adsorbed radical ions so produced have been identified through the hyperfine structure of the e.s.r. spectra. The course of the temperature variation of the spectra and that of the microwave power saturation curve were interpreted in terms of the nature of the adsorption process. The ability to vary the number of electron acceptor sites which were identified with decationated sites in the crystalline zeolite lattice facilitated the study of isolated free radicals present in the diamagnetic zeolite matrix. The properties of such electron acceptor sites are discussed and their implication to heterogeneous surface catalysis is examined.

Introduction

In recent years, the discovery of synthetic crystalline zeolites with highly porous structures has aroused a considerable interest in the field of physical adsorption and especially in the study of gas–solid interfaces. Mainly, this is due to the crystallographically well-defined structure of these porous crystals and also to some knowledge of the electronic properties of the surface. However, the most important characteristic of these crystals is that it is possible to vary the electronic structure of the surface by simply substituting in the lattice various cations of different sizes and charge while the lattice remains unchanged. Provided the cations do not differ largely in size, their location can be assumed to be the same in the lattice. This, then results in the variation of the electrostatic field or the field gradient on the surface, which in turn determines the interaction at the gas–solid interface.

The physical properties of these gas–solid systems have been studied not only through the classical adsorption technique but also with other types of measurements such as calorimetric, dielectric, electrical, infrared, and n.m.r. techniques. In particular, the Linde type X, A, and Y synthetic crystalline zeolites have been studied extensively in different cationic forms with various types of adsorbates.

In general, the interaction of an adsorbed molecule with any of the above types of lattices containing either alkaline or alkaline earth metal cations is weak, although the degree of interaction varies accordingly to the specific adsorbate–zeolite system. This type of interaction is usually referred to as a van der Waals adsorption and its total energy involves several types of contributions.

The relative importance of the particular type of interaction to the total adsorption energy has been examined. In most cases, depending on the polarity of the adsorbate molecule and the cation–zeolite system, the main interaction could be due to either dipole–electrostatic field, dipole–induced dipole, dispersion, polarization, or quadrupole interactions.

In these types of interactions, the perturbation of the electronic wave functions of the adsorbate at the interface is relatively small and adsorption (except sometimes at high temperatures) is usually found to be reversible, characterized by low activation energies.

However, in cases where the adsorbed molecule is very highly polarizable, such as ethylene, the perturbation of the surface is much stronger and, hence, the electronic structure of the molecules changes. Also when transition metal cations are present in the lattice, such as Cu^{++} and, for example, NH_3 is adsorbed, the interaction is fairly strong and irreversible. These cases could be termed as chemical adsorption in contrast to the previously discussed case of physical adsorption.

It is the object of this paper to present evidence that another type of adsorption can take place in these porous crystals when present in certain cationic form and after appropriate thermal treatment. This type of reaction, which involves rather easily ionizable organic molecules, is carried out through an electron transfer in the interface, resulting in the formation of ion radicals in the zeolite.

Electron transfer reactions have been observed earlier between basic aromatic hydrocarbons and $SbCl_5$. Originally, Hilpert and Wolf[1] observed the formation of colored solids in the reactions of aromatic hydrocarbons with $SbCl_5$. Later, Weissman, De Boer, and Conradi[2] demonstrated that the compounds of $SbCl_5$ with anthracene, tetracene, and perylene are paramagnetic with typical (e.s.r.) exchange narrowed lines. They suggested that singly charged positive ions are responsible for at least part of the observed paramagnetism.

This postulation was based on the similarity of the hyperfine structure of aromatic positive ions in H_2SO_4 solutions and that of aromatic hydrocarbon–$SbCl_5$ complexes dissolved in $POCl_3$. Further, Aalbersberg and his co-workers,[3] in their spectroscopic studies of

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(2) S. I. Weissman, E. De Boer, and J. Conradi, J. Chem. Phys., **26**, 963 (1956).

(3) W. Aalbersberg, G. J. Hoijfink, E. L. Mackor, and W. P. Weijland, J. Chem. Soc., 3055 (1959).

aromatic hydrocarbons–SbCl$_5$ mixtures, found that electron transfer from the hydrocarbon took place and that monopositive aromatic ions were formed in solution. More recently, Blomgren and Kommandeur[4] have shown that these systems form suspensions of small particles and the observed aromatic ions are present only in the solid. Also recently, electron transfer reactions of anthracene and perylene adsorbed on a silica–alumina amorphous catalyst support have been observed by Rooney and Pink.[5] In our experiments, the electron transfer takes place from a donor molecule to the zeolite lattice and an analogy can be drawn between the electron-abstracting properties of SbCl$_5$ discussed above and vacant electron sites present in the zeolite system.

In accord with previous work of electron transfer reactions in donor–acceptor molecular complexes, the purpose of this communication is to report a new type of acceptor with crystalline structure, having well defined electron-accepting sites in the lattice. The number of these electron-accepting sites can be varied as desired.

Experimental

A. Crystallographic Structure of Samples and Preparation.— The structure of the NaX and NaY zeolites has been shown[6,7] to consist of cuboctahedral cavities, which are joined together in a tetrahedral coordination like the carbon atoms in the diamond structure. This arrangement results in a series of channels interconnected through large openings. Each cavity has a free diameter of 12–13 Å. and is connected to four other similar cavities through common openings tetrahedrally arranged. These openings consist of 12 silica and alumina tetrahedra giving a free diameter of 8–9 Å. Further small cavities exist in the structure, but they are not available to large molecules (i.e., they can only accommodate a few water molecules). With every (AlO$_4$)$^-$ unit a monovalent cation is associated in order to give electrical neutrality in the crystal. The position of the cations has been defined and, accordingly, they are classified[7,8] into three types of cation sites in the crystal lattice. These are sites associated with the double six-membered and single six-membered rings accommodating up to 16 and 32 cations, respectively, per unit cell and the rest of the cations (up to 48), being more weakly bound to the lattice, are distributed in the large cavities.

By an isomorphous replacement during synthesis of Al for Si, it is possible to obtain a zeolite and the same framework structure as the X type but with a much smaller cation density. This also results in a much higher thermal stability of the NH$_4$$^+$Y as compared to the NH$_4$X type, which, during thermal activation in vacuo, loses its crystalline structure. The Linde type X and Y zeolites were used in the Na$^+$ and NH$_4$$^+$ cationic form. The composition of the unit cell for the Na$^-$ form of X and Y type zeolites is given, respectively, by the chemical formulas as Na$_{88}$[(Al$_2$O$_3$)$_{88}$-(SiO$_2$)$_{104}$] and Na$_{56}$[(Al$_2$O$_3$)$_{56}$(SiO$_2$)$_{136}$] for the anhydrous state.

The NH$_4$$^+$ form was prepared by using the usual ion-exchange techniques and by contacting the Na$^+$X or Na$^+$Y zeolite with an aqueous solution of NH$_4$NO$_3$.

The outgassing of the samples was performed in a conventional vacuum system equipped with an ion gage, liquid nitrogen cold trap, and mercury diffusion pump. To avoid grease vapor in the system, metal valves were used. A typical dehydration procedure, for example, for the NaX or NaY zeolites samples, was to evacuate, first slowly, the samples in Pyrex tubes and then slowly to raise the temperature up to 500°, while evacuating, to allow the sample to degas at this temperature, and then to remain in vacuo at least for 24 hr. at pressures near 10^{-6} mm.

Then the samples were sealed under vacuum and transferred to a drybox where the adsorption experiments were performed.

B. Adsorption of Donor Molecules on Zeolites.— The adsorption of the various molecules with electron-donating properties on the zeolite polycrystalline powders was done by contacting the degassed samples with a solution of the particular hydrocarbon, either in n-heptane or in chloroform.

The absorbates used were 1:1 and 1:2 diphenylethylene ((C$_6$H$_5$)$_2$C=CH$_2$), triphenylamine ((C$_6$H$_5$)$_3$N), quinoline, perylene, p-phenylenediamine, and aniline.

The chemicals used were "reagent" grade and they were dried over molecular sieve adsorbent.

A typical adsorption experiment was to transfer the degassed samples to small stoppered flasks inside the drybox in a dry nitrogen atmosphere free from oxygen and then, after the appropriate amount of solution was added, the samples were well stirred to effect a uniform adsorption. The amount of adsorption was determined by measuring the concentration of the solution before and after adsorption spectrophotometrically. It was found that by exposing the samples, before adsorption, to the vapor of the solvent, for example n-heptane, more accurate measurements were obtained. This is due to the adsorption of solvent itself on the zeolite (~30% weight). To the flasks, where the adsorption was done, small 5-mm. o.d. side Pyrex tubes were attached, where the zeolite, after adsorption was transferred for the e.s.r. measurements. The degassed samples, in the pure solvent, were completely colorless. On adsorption, various colors were developed, depending of course on the amount of adsorption and the type of adsorbate. In general, most of the intensity of the colors was developed within a few hours, but equilibrium was approached, as it was indicated by e.s.r. measurements, at different time intervals after 24 hr.

C. E.s.r. Measurements. (a) E.s.r. Apparatus Used.— The e.s.r. measurements were performed in a Varian spectrometer (Model V-4500) operating at 9.5 kMc./sec. and using the multipurpose cavity. The magnetic field was modulated at 100 kc./sec., and was measured by a proton magnetic resonance gauss meter. Varian conventional low temperature equipment was used. Low microwave powers were obtained with the Varian matching low power cavity.

(b) Measurement of Free Radical Concentrations.— The technique deveoped by Singer[9] was used to determine spin concentrations. A single crystal of ruby was used as the internal standard, which remains in the cavity at all times. This ruby is calibrated with a single crystal of CuSO$_4$·5H$_2$O of known susceptibility. If the shape of an e.s.r. line is closely Lorentzian, similar to that of CuSO$_4$·5H$_2$O, the paramagnetic susceptibility of the unknown can be obtained. The static spin susceptibility can be obtained from the expression

$$\chi_0 = \frac{48}{\pi w^2 \overline{H_1^2}} \int_0^\infty P_a \, dH_0$$

where w is the angular frequency of the rf. field of amplitude H_1, and P_a is the power absorbed by the sample. The gyromagnetic constant γ is given by the spectroscopic splitting factor g and the Bohr magneton, by the expression $\gamma = (\beta/h)g$. Then χ_0 is proportional to the area of the adsorption curve, of power P_a and static magnetic field H_6.

In order to apply these equations, saturation and skin effects must be absent and the line width should be smaller than H_0. To determine the number of spins (N) from the measured quantity χ_0 the nature of the paramagnetic species must be known. The mechanism by which the energy levels of the spin system are thermally populated in a magnetic field has to be known too. In the case, where thermally activated paramagnetism is absent, N is related to χ_0 by the expression, for the Curie law

$$\chi_0 = \frac{N g^2 \beta^2 S(S+1)}{3kT}$$

where, for free radicals with free spins, the spin quantum number $S = \frac{1}{2}$. However, for activated paramagnetism, expressions involving exponential dependence of N to the activation energy must be used.

As to the nature of spins, it can be assumed that, in the zeolite–radical systems, there is a ground doublet paramagnetic state with a free spin close to $\frac{1}{2}$. This is a reasonable assumption since the e.s.r. spectra obtained for certain organic molecules adsorbed on zeolites are very similar to those obtained for the same molecules in concentrated sulfuric acid where the positive ion radical is formed. Further, the g-values of the charge-transfer zeolite complexes are very close to the free spin value.

(c) Measurement of the Relaxation Times T_1, T_2.— The saturation of the samples was treated according to the "homogeneous broadening" mechanism, which includes dipolar spin-spin interaction, spin-lattice interaction, and other types of mechanisms, which are fluctuating rapidly compared with the time required for a spin transition. The progressive saturation method used by Bloembergen, et al.,[10] was used to determine T_1. The saturation parameter $Z(W_0, H_1)$ is given by

$$Z(w_0, H_1) = \frac{\chi''(w_0, H_1)}{\chi_0(w_0, 0)} = \frac{1}{1 + \frac{1}{4}\gamma^2 H_1^2 T_1 T_2}$$

The function $\left[\dfrac{\chi_0''(W_0, 0)}{\chi''(W_0, H_1)} - 1\right]$ is plotted against the radio-

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(5) J. J. Rooney and R. L. Pink, Proc. Chem. Soc., 70 (1961).

(6) D. W. Breck, W. G. Eversole, R. M. Milton, and T. L. Thomas, J. Am. Chem. Soc., **78**, 5963 (1956).

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(8) D. C. Freeman, Jr., and D. N. Stamires, J. Chem. Phys., **35**, 799 (1961).

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(10) N. Bloembergen and S. Wang, Phys. Rev., **93**, 72 (1954).

[Number of $(C_6H_5)_3N$ molecules in contact with 1 g. of zeolite] $\times$ 10^{-18}.
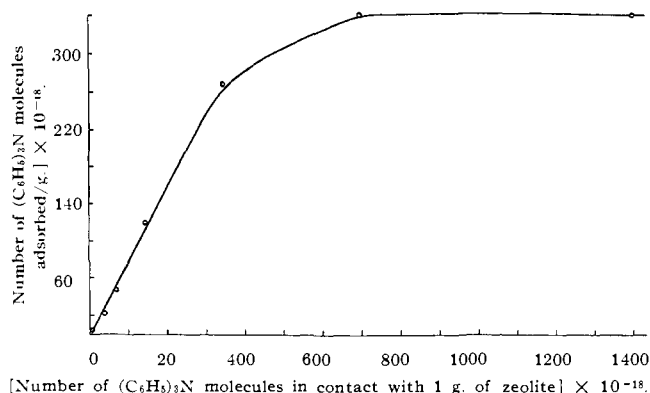
Fig. 1.—Room temperature isotherm of $(C_6H_5)_3N$ adsorption from n-heptane solutions on decationized Y zeolite.

frequency field intensity H_1 in a logarithmic form since

$$\log\left[\frac{\chi_0''(w_0,0)}{\chi''(w_0,H_1)} - 1\right] = 2\log H_1 + \log\left[\frac{\gamma^2}{4}\,T_1T_2\right]$$

The plot gives a straight line and, from the intercept, T_1 and T_2 can be obtained if H_1 is known. For the calibration of H_1 we used three samples of synthetic rubies containing different concentration of Cr^{+3}. The spin-lattice relaxation time (T_1) has been measured for these samples very accurately by the spin-echo method and was found to be independent of Cr^{+3} concentration in the range 0.002 to 0.1 atom Cr to the rest of Al at room temperature. Accordingly, T_1 was determined to be 3×10^{-1} sec. After the susceptibility of the ruby was measured as a function of the microwave power, this value of T_1 was used to determine H_1. The Varian low power matching cavity was used to attenuate, as low as 50 db., the available power.

Results and Discussion

A. The Adsorption and Electron Transfer of Triphenylamine $(C_6H_5)_3N$ on Decationized NH_4Y Zeolite.— Some of the properties of the decationized NH_4Y zeolite have been discussed previously.[11] Briefly, the thermal treatment of this type of zeolite results in the decomposition of the NH_4 ions to gaseous ammonia and protons in the lattice. The high reactivity of these protons has been demonstrated by infrared spectroscopy[12] which indicated the combination of the protons with oxygens from the aluminosilicate framework to form hydroxyl groups. At temperature near $500°$, the hydroxyl groups are eliminated in the form of water. These two chemical reactions which take place in the crystal during thermal activation modify its internal surface structure and, consequently, the electric field. However, the crystallinity remains unchanged and these crystals show normal adsorptive capacities for various gases.

Nevertheless, when the temperature of activation exceeds $1000°$, the crystal structure collapses and both the adsorption properties and X-ray structure disappear.

In the experiments described here, decationized NH_4Y zeolites, activated at $500°$ under vacuum, were used; they were highly crystalline with normal adsorptive capacity and were also diamagnetic. The concentration of paramagnetic impurities in these crystals was very small, in the order of a few parts per million.

The adsorption of $(C_6H_5)_3N$ from n-heptane solution at room temperature is shown in Fig. 1. In the low concentration region of the isotherm, the amount of adsorption is proportional to the concentration of $(C_6H_5)_3N$ in contact with the sample. A constant value of 3.4×10^{20} molecules/g. is obtained, corresponding to the maximum adsorption of $(C_6H_5)_3N$. Con-

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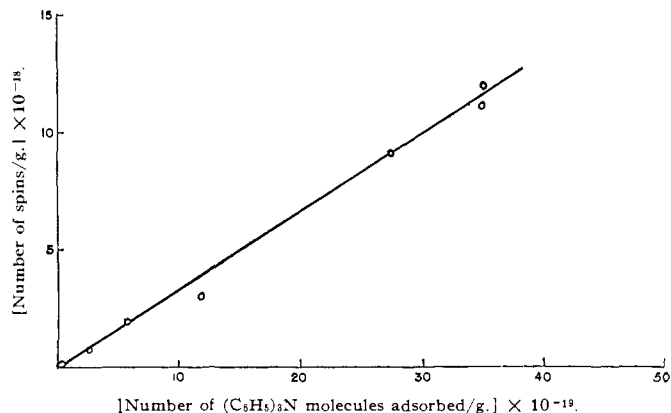

[Number of $(C_6H_5)_3N$ molecules adsorbed/g.] $\times$ 10^{-19}.

Fig. 2.—Increase in number of spins with adsorption of $(C_6H_5)_3N$ (n-heptane solution) on decationized Y zeolite at room temperature.

sidering the structure of the unit cell of this zeolite, it appears that about eight $(C_6H_5)_3N$ molecules are adsorbed per unit cell or one in each of the large cavities. The shape of the isotherm is typical of the van der Waals type. However, because of the nature of the internal crystal surface of the zeolite, the conventional interpretation of an isotherm of this type is not applicable. The maximum quantity of $(C_6H_5)_3N$ absorbed is determined by the available volume of the individual cavities as it compares with the effective volume of an individual $(C_6H_5)_3N$ molecule. In addition, the volume of the solvent molecules have to be considered in the filling of the crystal cavities. The color of the samples varied from pale bluish violet in the low concentration of $(C_6H_5)_3N$, to black in the highest concentration. It was found that the adsorption of $(C_6H_5)_3N$ on the decationized zeolite produced strong e.s.r. signals. The intensity of the resonance is proportional to the amount of $(C_6H_5)_3N$ adsorbed. The increase of the number of free radicals formed with increasing adsorption is shown in Fig. 2. The linear increase observed indicates that even at the highest adsorption of $(C_6H_5)_3N$, there is no saturation in the number of spins.

However, this does not mean that there is still a number of sites which could pick up electrons from $(C_6H_5)_3N$ but there are not enough $(C_6H_5)_3N$ molecules adsorbed to give up these electrons. This is illustrated by comparing the following numbers: the number of electron-accepting sites as measured from the cation density in the zeolite is about 2×10^{21} sites/g. The number of adsorbed $(C_6H_5)_3N$ molecules (saturation) is 3.4×10^{20}/g., and the maximum number of spins obtained, when the crystals were saturated with $(C_6H_5)_3N$, is 1.2×10^{19} spins/g. Therefore, the number of $(C_6H_5)_3N$ molecules adsorbed is larger than the number of free radicals formed from the interaction of $(C_6H_5)_3N$ with the acceptor sites in the crystal.

However, comparing those numbers, one has to consider certain other facts which probably determine the relative magnitudes of these numbers. First, the rather large size of the $(C_6H_5)_3N$ molecule restricts its adsorption only to the large cavities in the Y zeolite structure. This is in accord with our experimental results. Secondly, the electron-accepting sites in the zeolite, as it will be discussed later, are decationized $(AlO_{4/2})^-NH_4^+$ sites, namely three-coordinated aluminum $(AlO_{3/2})$. The number of such sites in the large cavities corresponds to one per cavity. This would give about 3×10^{20} spins/g., which is about 20 times larger than the experimental value. Another point, which has to be considered here, is that certain steric hindrance probably exists, which makes difficult the close approach
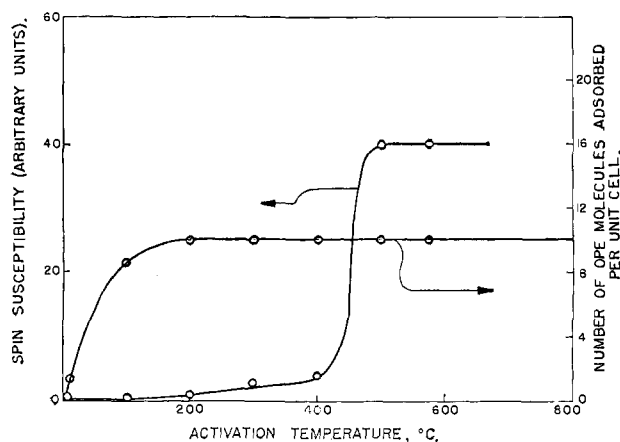
Fig. 3.—The effect of activation temperature of decationized Y zeolite on the adsorption of diphenylethylene and the increase of number of spins with adsorption at room temperature.

to the $(C_6H_5)_3N$ to the electron acceptor site $(AlO_{3/2})$. All these effects discussed above tend to make the number of free radicals smaller than the absorbed $(C_6H_5)_3N$ or the decationized sites. It should be noted here that similar effects have been observed in other quite different systems. For example, in perylene–iodine charge transfer complexes,[13] the concentration of neutral perylene molecules is about 30 times greater than the number of perylene free radicals formed.

Another suggestion is that, for every free radical a certain number of unreacted molecules is required, probably for stabilization. Also it may involve reactions such as $2(C_6H_5)_3N \rightarrow (C_6H_5)_3N^{++} + (C_6H_5)_3N$, which of course will decrease the number of measurable free radicals.

B. The Effect of the Temperature of Activation of the NH_4Y Zeolite on the Adsorption and Electron Transfer of Donor Molecules.—As it will be pointed out later, any molecule with low ionization potential (good donor) and with reasonable small sizes, in order to be able to enter the crystal cavities, will form a charge transfer complex with the decationized zeolite. One of these types of molecules is diphenylethylene (DPE).

The NH_4Y zeolite samples (1 g. each) were heated under vacuum at various temperatures for the same period of time (about 12 hr.) and then contacted at room temperature with a concentrated solution of DPE (about 4×10^{21} DPE molecules/g.). After equilibrium was reached, the spin susceptibility and the amount of DPE absorbed were measured. The results are shown in Fig. 3. For the adsorption of DPE only the elimination of the water in the crystals is required in order to allow the DPE molecules to enter the cavities. Near 200°, the majority of water molecules have been desorbed and, then DPE molecules are able to enter the crystals.

However, there is no electron transfer taking place up to almost 400°. Near 500°, there is an enormous increase in the spin susceptibility and it remains constant for higher activation temperatures. It appears that temperatures above 400° are required in order to form the electron-acceptor sites, which are responsible for the complex formation.

A similar behavior was found for $(C_6H_5)_3N$; for example, NH_4^+Y zeolite activated at ~200° adsorbs $(C_6H_5)_3N$ but exhibits no paramagnetism. The changes taking place in the aluminosilicate framework during the decationization of the NH_4Y zeolite will be discussed later.

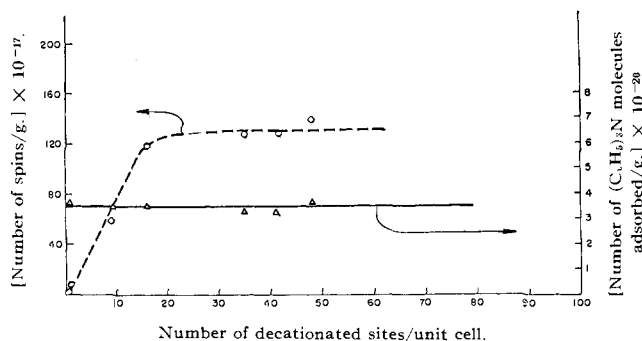(13) L. S. Singer and J. Kommandeur, J. Chem. Phys., **34**, 133 (1961).

Fig. 4.—The effect of decationization of the Y zeolite on the amount of $(C_6H_5)_3N$ adsorption and the number of spins.

C. The Variation in the Spin Concentration with the Number of Decationized Sites Present in the Lattice.—Again in this experiment, the samples containing various amounts of NH_4^+ ions were heated to 500° under vacuum for at least 12 hr. Then they were contacted with concentrated solution of $(C_6H_5)_3N$ and the concentration of free radicals formed were measured. The results are shown in Fig. 4 where the number of spins and $(C_6H_5)_3N$ molecules adsorbed are plotted as function of the number of decationized sites per unit cell. The amount of adsorption of $(C_6H_5)_3N$ is independent of the decationization. This constant amount of adsorption is about 3.4×10^{20} molecules/g., which corresponds to about 8 molecules/unit cell. This is the same number found in the isotherm of $(C_6H_5)_3N$ adsorbed on decationized zeolite. This indicates that the creation of three-coordinated aluminum in the zeolite does not destroy its crystal structure, as both the NaY and decationized Y adsorb equal amounts of $(C_6H_5)_3N$. The concentration of the formed free radicals, on the other hand, varies with the amount of decationization. The number of spins increases linearly up to almost 16 decationized sites in the unit cell. For higher concentrations, the number of spins remain unchanged. This indicates that only the first 16 exchanged Na^+ for NH_4^+ ions are effective in creating three-coordinated aluminum sites, which determine the number of $(C_6H_5)_3$-N free radical formed. Introduction of larger amounts of NH_4^+ ions form more decationized sites, but those are not available to adsorbed $(C_6H_5)_3N$ for electron transfer. It appears then, that the first ions to be exchanged must be located in the large cavities of the crystal. According to the classification[7,8] of the cations in the unit cell, which was based on their position in the lattice, there are three types. In the NaY structure, there are 16 Na^+ (type I) located in the plane of the six-member oxygen rings, 32 (type II) located in the double six-member oxygen rings, and the last eight cations (type III) are randomly located in the large cavities. The cation sites, associated with the last eight cations, are involved in the electron transfer process, together with some other cation sites located in the windows of the large cavities, which the triphenylamine molecules can easily approach. One might conclude then, that for small amounts of cation exchange, the type III are first exchanged and then successively the other types. This is important when small amounts of various cations are introduced in the crystal with the purpose to study their magnetic, surface and catalytic properties, or e.s.r. spectra.

It should be noted that, although this number of spins appears to increase with increasing number of decationized sites, their magnitudes differ considerably; i.e., the maximum number of spins ever obtained is about 1.5×10^{19} as compared to 2×10^{21} decationized sites.
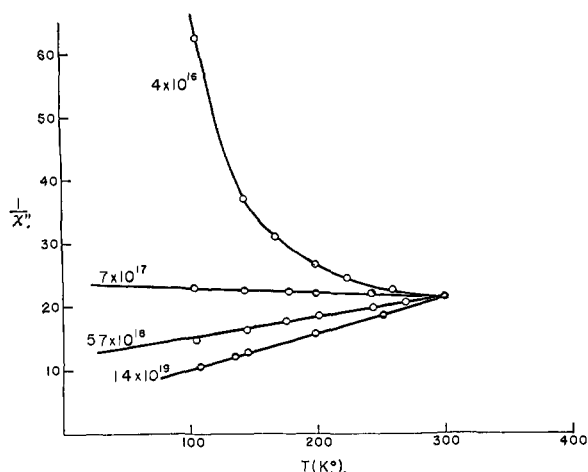
Fig. 5.—The variation of reciprocal spin susceptibility with temperature. For various concentrations of $[(C_6H_5)_3N^+]$ cation radicals on decationized Y zeolite.

Assuming that only 8 out of 56 cations are effective in electron transfer, then the 2×10^{21} decationized sites/g. is reduced to 2.8×10^{20}, which is still larger, by a factor of 20 from the maximum spin concentration observed.

It seems reasonable then to assume that, although by increasing the number of decationized sites in the crystal the number of free radicals also increases, the number of spins remains always smaller (~20 times) than the number of either the available electron transfer sites or the unreacted $(C_6H_5)_3N$ molecules. Some of the reasons which are probably causing this effect have been discussed in the first section.

D. Temperature Variation of the Spin Susceptibility for Various Concentrations of Triphenylamine Free Radicals.—The reciprocal of integrated spin susceptibility as a function of absolute temperature for four different concentrations of $(C_6H_5)_3N$ adsorbed on about 90% decationized Y zeolite is shown in Fig. 5. The intensities of the e.s.r. adsorption for the four concentrations have been normalized to one value at 300°K. This was done in order to be able to display simultaneously the effect of temperature on the four concentrations.

The spin susceptibility for samples $(1.4 \times 10^{19}$ and $5.7 \times 10^{18})$ varies according to the Curie–Weiss law, having a rather large Weiss constant. However, at the next lower concentration (7×10^{17}), a temperature-independent spin variation is observed. By further decreasing the concentration of free radicals (4×10^{16}) the susceptibility decreases with decreasing temperature; quite in contrast with the high concentrated samples. It appears then, that there is a trend for a decrease in the number of spins with the lowering of the temperature; however, this trend is less obvious in the highly concentrated samples and strongly manifested in the less concentrated ones. Then, the deviation of the highly concentrated sample from the Curie law is assumed to be due to this general trend rather than to the presence of magnetic field effects.

The logarithm of the susceptibility of the 4×10^{16} spins sample plotted as a function of reciprocal absolute temperature gives a straight line with an activation energy of about 2.3 kcal./mole. Further, we have tried, unsuccessfully, to fit the experimental curve for this concentration to the equation

$$\chi'' = 1/T[\exp(+E/kT) + 3]$$

Here, the e.s.r. absorption intensity χ'' is expressed in terms of the absolute temperature and the activation energy E, which separates, in a pairwise spin correla-

tion, the ground singlet state from the associated triplet state.

This equation, however, has been used to explain similar temperature effects in the case of amine–tetracyanoquinone complexes where the paramagnetic species were assumed to be small amounts of impurities in the crystals.

In our case, the presence of well resolved hyperfine structure in the less concentrated samples does not suggest the presence of paramagnetic impurities.

A possible mechanism, explaining this general decrease in the number of spins at lower temperatures, is to assume an existing equilibrium between paramagnetic and diamagnetic $(C_6H_5)_3N$ molecules. This may involve the equilibrium

$$2(C_6H_5)_3N^+ \mathrel{\underset{\longleftarrow}{\longrightarrow}} (C_6H_5)_3N^{++} + (C_6H_5)_3N + Q$$
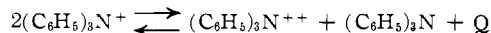
where two free radicals interact to give the ion $(C_6H_5)_3N^{++}$ and a neutral $(C_6H_5)_3N$ molecule. The fact that, at low spin concentrations, the ratio $(C_6H_5)_3N/(C_6H_5)_3N^+$ in the crystal is close to unity suggests that the above equilibrium may exist. The lowering of the temperature then will favor the formation of diamagnetic $(C_6H_5)_3N^{++}$ ions. This type of equilibrium might still exist in the highly concentrated samples; however, the presence of an excess of unreacted $(C_6H_5)_3N$ in the crystal will decrease considerably the number of $(C_6H_5)_3N$ ions and the formation of $(C_6H_5)_3N^+$ will be favored. In such a system, the decrease of temperature probably will have a twofold effect. first, to increase the susceptibility according to Curie law; and, secondly, a small decrease due to the equilibrium discussed above. The relative magnitudes of these two opposing effects determine the general observed variation of spin susceptibility with lowering of the temperature. It is of interest to note that the susceptibility of the sample with 7×10^{17} spins/g. is independent of temperature. For lower concentrations, the effect of temperature on the equilibrium, rather than on the paramagnetism of the free radicals, is the dominating factor.

E. Relaxation Times T_1 and T_2 of the $(C_6H_5)_3N^+$ Free Radical in the Zeolite Crystal.—The spin-lattice relaxation time T_1 for various concentrations of $(C_6H_5)_3N^+$ ion radicals in the zeolite crystals has been determined at room temperature and is shown in Fig. 6 and Table I.

The T_1 at the beginning decreases rapidly as the concentration of $(C_6H_5)_3N^+$ increases, but toward the highest values of spins it approaches almost a constant value (~3 $\times$ 10^{-6} sec.). The highest value (~1.2 $\times$ 10^{-5} sec.) is observed for the lowest concentration of $(C_6H_5)_3N^+$ ion radicals. It appears then, that the spin–lattice interaction increases as the porous structure of the crystals becomes more populated with free
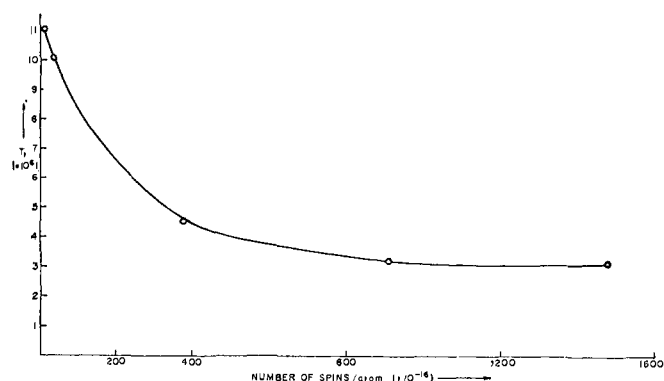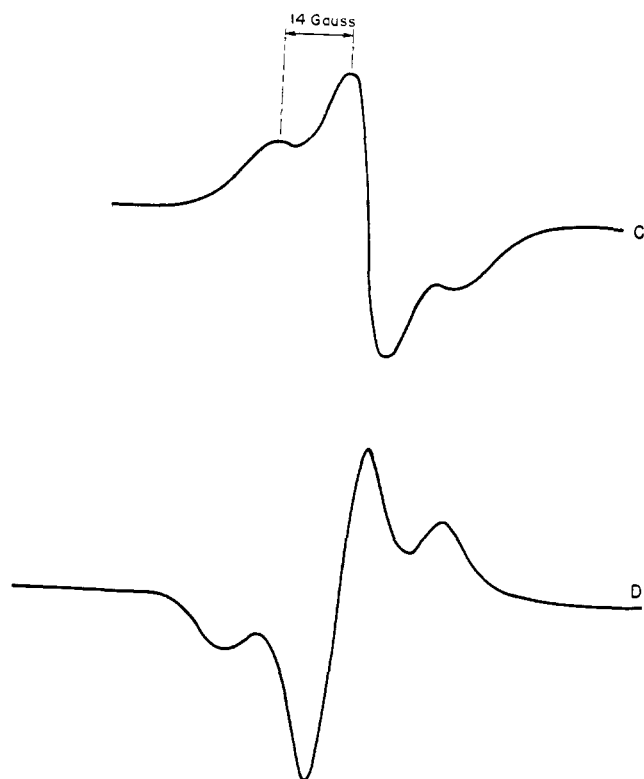

Fig. 6.—The effect of concentration of $[(C_6H_5)_3N^+]$ cation radicals on the spin-lattice relaxation time (T_1) at room temperature.

Fig. 7.—E.s.r. absorption of $[(C_6H_5)_3N^+]$ cation radical on decationized Y zeolite (C); e.s.r. of the $(C_6H_5)_3N–I_2$ complex at 25°.

radicals. To understand this increase of the interaction, one must keep in mind that the $(C_6H_5)_3N$ ion radical is located in the pores, together with solvent (n-heptane) and also with neutral $(C_6H_5)_3N$ molecules.

TABLE I

SPIN-LATTICE AND SPIN-SPIN RELAXATION TIMES FOR $(C_6H_5)_3N$ IN DECATIONIZED Y ZEOLITE AT ROOM TEMPERATURE

Spins/g.	T_1, sec.	T_2, sec.
1.5×10^{19}	3.1×10^{-6}	5.9×10^{-9}
9.1×10^{18}	3.2×10^{-6}	4.6×10^{-9}
3.8×10^{18}	4.6×10^{-6}	1.8×10^{-9}
3.3×10^{17}	1.0×10^{-5}	1.8×10^{-9}
4.0×10^{16}	1.1×10^{-5}	1.8×10^{-9}

Thus, the relaxation mechanism of the $(C_6H_5)_3N^+$ probably then involves the molecules associated with the $(C_6H_5)_3N^+$ ion radical.

This is indicated further, since $(C_6H_5)_3N^+$ interacts strongly with $(C_6H_5)_3N$ molecules in a solution (accompanying paper). One, then, would expect T_1 to decrease as the number of unreacted $(C_6H_5)_3N$ molecules increases.

As will be discussed later, hyperfine structure in the e.s.r. of the $(C_6H_5)_3N^+$ can be distinguished even at the highest concentrations, thus suggesting that the type of interaction discussed above probably involves $(C_6H_5)_3N^+$ and $(C_6H_5)_3N$ molecules. Another way in which one might consider the decrease of T_1 with increasing concentration of radicals in the pores is the increase of $(C_6H_5)_3N$ in the pores as resulting in an increase of the viscosity of the liquid phase in the porous structure of the crystal. Then, through changes in the correlation time for the tumbling of the ion radical, T_1 decreases with increasing viscosity of the medium.

The effect of temperature for two different concentrations of $(C_6H_5)_3N^+$ is shown in Table II.

For both concentrations, T_1 decreases as the temperature is lowered however, a greater decrease in T_1 is observed for the highly concentrated sample, which has

TABLE II

| | 1.5×10^{19} spins/g. | | 4×10^{16} spins/g. | |
	300°K.	138°K.	300°K.	128°K.
T_1	3.1×10^{-6}	4.3×10^{-7}	1.2×10^{-5}	8.3×10^{-7}
T_2	5.9×10^{-9}	5.9×10^{-9}	1.5×10^{-9}	1.8×10^{-9}

the shortest relaxation time. In both cases, the decrease of T_1 is due to the freezing of the liquid phase in the pores of the crystals and, by reducing the number of degrees of freedom of the $(C_6H_5)_3N^+$ ion radical in the solid state, the spin–lattice interaction increases.

The values of the spin–spin relaxation time T_2 remains the same as the concentration of spin increases from 4×10^{16} to 3.8×10^{18} indicating that the spins are far removed from each other. However, when the concentration reaches 10^{19} spins the relaxation time increases, and the line becomes more narrow. This interaction may be due to an exchange narrowing. The temperature independency of the T_2 (Table II) is consistent with this point of view.

The spin–lattice relaxation time has been measured for another molecule, which can form an electron-transfer complex with decationated Y zeolite, namely diphenylethylene) $(C_6H_5)_2C=CH_2$. This gives a single e.s.r. line ($\sim 10^{18}$ spins/g.) from a n-heptane solution and $T_1 = 4 \times 10^{-7}$ and $T_2 = 6 \times 10^{-9}$ sec. at room temperature. This small value of T_1 probably is due to the presence of the double bond in the molecule $(C_6H_5)_2C=CH_2$ which gives rise to strong intermolecular interactions in the adsorbed phase.

F. Magnetic Parameters of the E.s.r. Absorption Spectra.—When the $(C_6H_5)_3N^+$ ion radical is present in small concentrations in the decationized ($\sim 90\%$) Y zeolite, an e.s.r. line having three well resolved peaks is obtained (Fig. 7C). The line is symmetric and has a g-value of 2.0027 ± 0.0002. The three peaks are due to the interaction of the unpaired electron with the nuclear moment of N^{14} ($I = 1$) in the $(C_6H_5)_3N$ molecule. The three peaks have an intensity ratio of $1:2:1$. The hyperfine splitting constant is about 14 gauss and the over-all width of the line about 36 gauss. The three peaks in the hyperfine structure indicate that the free electron is located near the nitrogen atom in the $(C_6H_5)_3-N^+$ ion radical. This can be compared to the $Na_2^+-(SO_3^-)_2NO$ free radical which, in aqueous solution, gives an e.s.r. line with three peaks with a splitting constant of 13 gauss. Further, the electron-donating properties of the $(C_6H_5)_3N$ have been discussed elsewhere (accompanying paper) and it has been shown that it forms electron transfer complexes with good acceptors. Therefore, it is certain that the adsorption of $(C_6H_5)_3N$ on decationized zeolite results in the formation of $[(C_6H_5)_3N \cdot]^+$ positive cation radical. When the concentration of free radicals is increased, the line is slightly broadened and the two outside peaks from the center of the line decrease in intensity and appear as weak shoulders on the single line. This behavior is only found when successive amounts of $(C_6H_5)_3N$ are allowed to intact with a ($\sim 90\%$) decationized Y zeolite. However, if a small dilution of spins is obtained by allowing an excess of $(C_6H_5)_3N$ to interact with a sample of Y zeolite, which has only a small fraction of cation sites decationized, then only one single e.s.r. line is obtained with the two weak shoulders on the low and high field sides observed only in the high concentrations. The low concentrations exhibit only single lines showing not even weak shoulders. It appears, then, that the resolution of the hyperfine structure in the two series of experiments described above does not depend on magnetic effects, which cause broadening. but rather on the amount of unreacted $(C_6H_5)_3N$ present in the pores of crystal. The
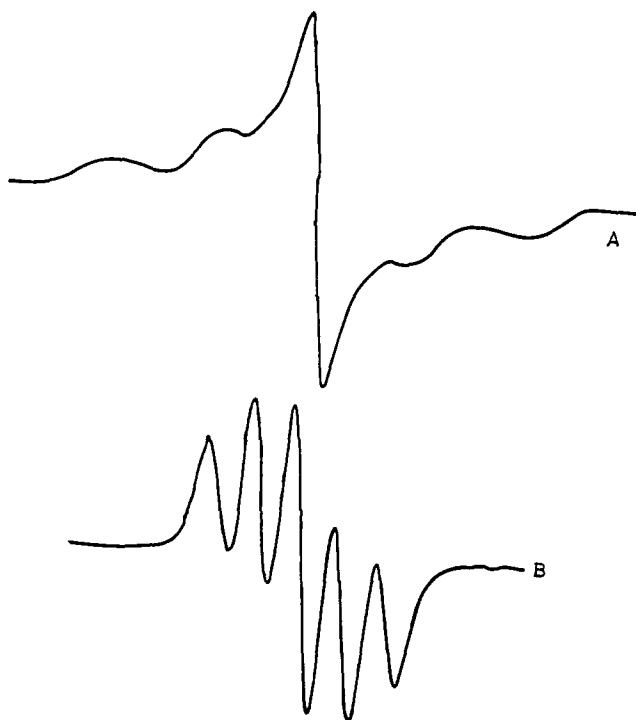
Fig. 8.—E.s.r. of DPPH adsorbed on Vycor from benzene solution (A); e.s.r. of DPPH in benzene solution (B).

Fig. 9.—E.s.r. of perylene in (A) concentrated H_2SO_4; (B) I_2 at 135°; and (C) adsorbed on decationized Y zeolite from n-heptane solution at room temperature.

$[(C_6H_5)_3N\cdot]^+$ radical probably interacts with the $(C_6H_5)_3N$ molecules and, as a result, delocalization of the electron causes the hyperfine structure to disappear. Further, excess $(C_6H_5)_3N$ in the pores will reduce the motional degrees of freedom of the $[(C_6H_5)_3N\cdot]^+$ ion radical considerably, thus decreasing the averaging of the anisotropy of the complex and, consequently, eliminating the hyperfine structure.

The perturbation of the surface forces on an adsorbed radical is illustrated in Fig. 8, where DPPH from a benzene solution has been adsorbed on Vycor glass (highly porous medium). The e.s.r. of DPPH in solution is shown in spectrum A and that of DPPH adsorbed on Vycor, in spectrum B. It appears that the effect of surface on the spectrum is to broaden the outside peaks considerably, leaving the middle peak almost unchanged. A similar type of anisotropic broadening has been observed in DPPH dispersed in cements and has been treated as a viscosity effect.

The effect of the freedom of the adsorbed free radical on a surface on the resolution of its hyperfine structure is further illustrated by the adsorption of $(C_6H_5)_3N$ from the vapor phase on decationized Y zeolite. The adsorption of $(C_6H_5)_3N$ was performed in a closed evacuated U-shaped tube where at one end was placed the zeolite and at the other the $(C_6H_5)_3N$. The tube was immersed in an oil bath at 200°. The adsorption was slow and the color, from pale blue at the beginning, turned slowly to black at higher adsorptions. The sample was taken out of the bath at various intervals and the e.s.r. of zeolite was measured at room temperature. In all stages of adsorption, a single e.s.r. line was obtained. The g value was close to that for free spin, but this line had a small asymmetry. However, after the adsorption was completed, the tube was opened in a nitrogen atmosphere and n-heptane was added to it at room temperature. This immediately resulted in the appearance of the hyperfine structure typical of $(C_6H_5)_3$-N adsorbed on decationized Y zeolite from n-heptane solutions. It appears then that the solvent reduces the adsorption forces existing in the interphase of $(C_6H_5)_3N$/zeolite so that the $(C_6H_5)_3N$ molecules gain a
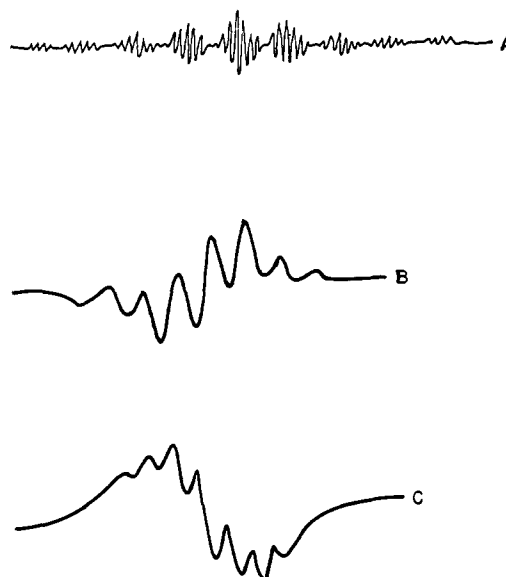
certain amount of motional freedom on the surface, which is expressed in the resolution of the hyperfine structure. This is very reasonable since the aluminosilicate surface has appreciable affinity for the benzene groups in the $(C_6H_5)_3N$ molecule, owing to interaction between the hydrogens in the $(C_6H_5)_3N$ and the oxygens of the crystal framework. Similar effects have been observed when, in the samples exhibiting the best resolved hyperfine structures of $(C_6H_5)_3N$-n-heptane-zeolite systems, the solvent is pumped out, or the sample cooled to a sufficiently low temperature so that the solvent in the porous crystals becomes solid. Both of these treatments result in broadening and line anisotropy.

G. Adsorption of Other Types of Donor Molecules on Decationized Zeolite.—It was found that aniline adsorbed on decationized zeolite from n-heptane or carbon tetrachloride solution gives a symmetric e.s.r. line ($g = 2.002$), which has a hyperfine structure of three equally spaced peaks. The hyperfine splitting constant is about 10 gauss, which is similar to that of DPPH in solution. However, the adsorption intensity of the e.s.r. of aniline is very weak. This is probably due to the poor donating properties of this molecule. Perylene was also adsorbed on decationized zeolite from carbon tetrachloride solution and intense e.s.r. adsorption was obtained. In samples with small concentrations of perylene a hyperfine structure was partially resolved as shown in Fig. 9C. The ability of perylene to form electron-transfer complexes has been shown previously[13] in connection with various types of electron acceptors. In concentrated sulfuric acid the hyperfine structure, shown in Fig. 9A, is due to the positive ion radical of perylene,[14–16] where the paramagnetic hole interacts with the hydrogens in the molecule. This spectrum has been included here for comparison with the spectrum of perylene-I_2 and perylene-zeolite. Perylene donates also an electron to the I_2 molecule (in the molten state) to form the positive ion radical. Although the hyperfine structures are not completely resolved, the three spectra are definitely similar. Further,

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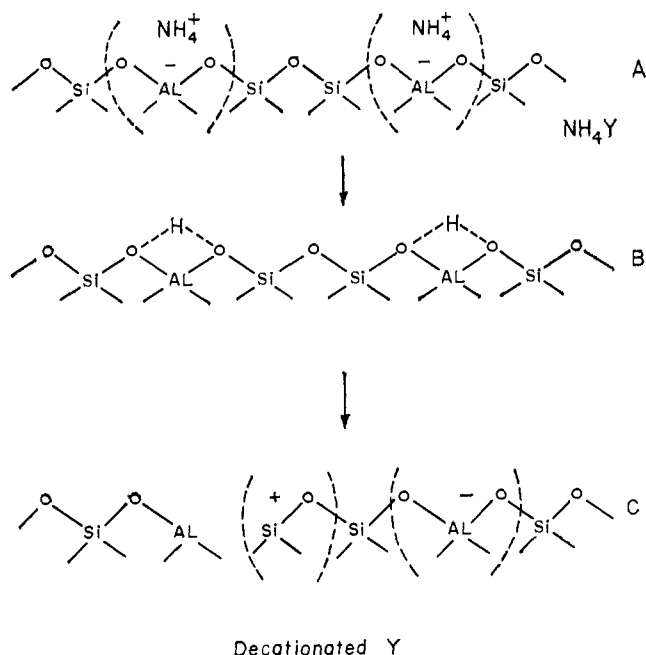
Decationated Y

Fig. 10.—A possible mechanism for the elimination of NH_4^+ ions by heating in the NH_4Y zeolite.

the spectrum of perylene adsorbed on decationized zeolite is very similar to both of the spectra discussed above. Here, as in all cases of resolved hyperfine structure, oxygen adsorption broadens the e.s.r. reversibly. It can be seen that the decationized sites in the zeolite crystals act as electron acceptor sites and form electron transfer complexes with molecules which have reasonably low ionization potential.

In all cases where electron transfer takes place in the crystals at the adsorbate–adsorbent interface, we have an indication that only the e.s.r. of the cation radical can be observed. The electron taken up by the acceptor site in the crystal framework has not been observed. This may be due to the short relaxation times, or complete delocalization in the lattice, where a variety of crystalline fields exist, thus broadening the e.s.r. line sufficiently that it cannot be observed. At this point, it is of interest to contrast the electron affinity of the acceptor sites in the zeolite crystals with other good donors such as iodine. Certainly a fair comparison is not possible since other factors besides electron affinity determine the ability of forming electron-transfer complexes.

However, iodine, which has been shown to be one of the best acceptors in electron-transfer complexes, does not form paramagnetic complexes when mixed, at room temperature, with donors such as aniline, naphthalene, diphenylamine, or diphenylethylene; at elevated temperatures, e.s.r. signals begin to appear. However, these molecules form complexes with the decationized zeolite at room temperature. It appears, then, that the electron acceptor sites in the decationized Y zeolite are at least as good acceptors as iodine.

H.   Structure of the Decationized NH₄Y Zeolite.—Based on the previous discussion and on the fact that ammonia gas and water are eliminated from the zeolite during heat treatment, and also that the resulting structure is diamagnetic, the following mechanism is proposed for the formation of active sites responsible for the creation of radicals. One simplified two-dimensional representation of the basic lattice structure of the unheated NH_4Y zeolite is shown in Fig. 10A. The ammonium ions are associated with the $[AlO_4]^-$ cation sites separated by neutral $[SiO_4]$ units. During

the heating at low temperature the ammonium ions give protons and ammonia gas. Owing to their high reactivity, these protons attack the oxygens of the lattice and, as has been shown by infrared spectroscopy, form hydroxyl groups. An intermediate state can be represented by Fig. 10B showing that the protons form strong hydrogen bonds with the crystal lattice. However, at higher temperatures, the observed elimination of water results from the combination of a hydroxyl group with a proton, leaving a defect in the lattice. The resulting defect in the lattice is shown in Fig. 10C. Similar structures can be formed depending upon whether the water elimination involves two $(AlO_{4/2})^-$ units or two $(SiO_{4/2})$, or one of each. Nevertheless, the important point here is to show that the structure of the NH_4Y zeolite activated at high temperature ($\sim 500°$) contains three-coordinated aluminum ions derived from the initially four-coordinated units after elimination of a hydroxyl group. Previously,[11] a paramagnetic structure was postulated; however, it was proved[15] later that the paramagnetism was due to foreign species present in the crystals.

In structure C it appears that one in every two $(AlO_{4/2})^-$ units is converted from the four-coordinated state into a three-coordination situation. However, this is not necessarily so since, considering the non-linear structure of the lattice, it is possible that only a small fraction of the $(AlO_{4/2})^-$ units is in favorable position so as to make possible the elimination of water. The three-coordinated aluminum ion explains the formation of the free radicals since it has properties similar to $AlCl_3$ or $SbCl_5$ and behaves in a manner comparable to iodine. It appears then that an electron is transferred from the adsorbed molecule to the $(AlO)_{3/2}$ unit, possibly forming a charge transfer complex such as $[(C_6H_5)_3N]^+ [AlO_{3/2}]^-$ in the crystal. The $(AlO_{3/2})$ units constitute electron traps which are distributed evenly throughout the internal zeolite structure. The stabilization of the free radicals formed is due to the rigidity of the electron-accepting sites in the lattice of the crystal.

I.   Significance to Surface Catalysis.—The activated NH_4Y zeolite has been found previously[11] to be an active catalyst support in the isomerization reactions of hydrocarbons. Usually, these reactions take place at elevated temperatures, near 300°.

From the behavior of this type of zeolite at room temperature toward easily polarizable organic molecules, it can be assumed that the surface catalytic properties exhibited toward less polarizable molecules involve the same type of mechanism. That is, the adsorbed hydrocarbon on the surface is associated with $(AlO_{3/2})$ units forming some type of complex probably through a weak electronic interaction. At elevated temperatures, the appropriate activation energy is provided in order to form the positive charged radical after electron transfer.

This ion radical (carbonium ion) can then be considered as an activated intermediate in the catalytic process. Because of the open spacing of the crystals and the elevated temperature, the rate of transfer of molecules from the gas phase to the surface and vice versa is fairly high. Also the mobility of the molecules or ion radicals on the surface is expected to be high, thus resulting in an efficient catalytic reaction. However, the ability of the $(AlO_{3/2})$ unit to form charge-transfer complexes does not eliminate the possibility that in some catalytic reactions the first step may be the abstraction of the hydride ion $(H)^-$ from the organic molecule. Then the positive charged species formed can interact with a neutral molecule to form a free

radical. Further it has been shown[16] that the catalytic sites can be inactivated by chemisorption compounds such as quinoline. The decrease in catalytic activity is linearly related to the amount of nitrogen compound chemisorbed.

In our experiments we adsorbed quinoline on the activated zeolite and intense e.s.r. signals were obtained. Here again a charge-transfer complex simi-

lar to that formed by $(C_6H_5)_3N$ is formed in the crystal lattice. At present, it appears that the $(AlO_{3/2})$ electron traps in the crystal lattice are responsible, first for the strong adsorption of organic molecules with low ionization potential which form charge-transfer complexes and, secondly, for the catalytic activity of these types of crystals in heterogeneous catalytic hydrocarbon reactions.

Paramagnetic Resonance Absorption of γ-Irradiated Synthetic Zeolites

By Dennis N. Stamires and John Turkevich

A study has been carried out on the effect of γ-irradiation of synthetic zeolites. Sodium X and sodium Y zeolites and also decationated samples prepared from these were irradiated under vacuum at room temperature with doses up to 20 megaroentgens. Two types of e.p.r. signals were obtained. For the sodium Y and the sodium X zeolite a single line signal X_1 was found. It was 38.4 gauss wide with $g = 2.0200$, indicating that it is a hole; its intensity followed the Curie law. Heating above 350° caused the signal to disappear. The signal was decreased by oxygen gas, but the effect was reversible. Saturation does not take place with irradiation up to 14 megaroentgens. A pink coloration was also produced, but its behavior did not parallel that of the X_1 signal. For the decationated Y zeolite a six-lined e.p.r. signal was obtained by radiation. The separation between the lines was 5 gauss and the center of this signal was at $g = 2.0017$. Its intensity was independent of temperature and the signal annealed at about 500°. The signal is not affected by oxygen and its intensity saturates at an exposure of 3 megaroentgens; no coloration was observed. For partially decationated sites both X_1 and X_2 signals were observed. The X_1 signal is interpreted to be a hole located on the oxygen of the lattice while the X_2 is assumed to be due to an electron located near the Al^{27} nucleus that has been decationated.

Introduction

The nature of the various types of defects in solids produced by high energy irradiation has been successfully studied in many cases by the method of paramagnetic resonance.[1-3] These defects usually give rise to characteristic absorption spectra which have been used to study such defects. However, most of the defects are paramagnetic centers, and e.s.r. measurements provide very useful information about the type of defect, its environment, and crystal field symmetry. The host lattice plays an important role in formation and identification of the defects. First, nonparamagnetic structural changes in the lattice can modify the field symmetry near the paramagnetic center which, in turn, alters the e.s.r. spectrum.[4,5] Secondly, by incorporation (or present as an impurity) of atoms with magnetic nuclei in the lattice, nearby holes or electrons can be identified through hyperfine structures found in the e.s.r. spectra. Such is the case in the magnetic resonance of irradiated quartz,[2,3] where the paramagnetic hole is located near an aluminum atom (present as an impurity) which gives rise to a six-line hyperfine structure. We irradiated polycrystalline aluminosilicates, namely synthetic zeolites, with γ-rays where the quantity, position, and state of the aluminum in the alumino-silicate framework was known. By suitably modifying the coordination of the aluminum $[AlO_{4/2}{}^-]$ with the oxygens of the lattice, a hole can be produced at the $[AlO_{3/2}]$ unit which can trap an electron. This exhibits a characteristic e.s.r. with a hyperfine structure. On the other hand, when the aluminum is present in the original four-coordinated state which is isomorphous with the silicon present

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(3) D. S. Billington and J. H. Crawford, "Radiation Damage in Solids," Princeton University Press, Princeton, N. J., 1961.

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$(SiO_{4/2})$, a paramagnetic hole, but not an electron, is observed. This hole has no hyperfine structure and exhibits different magnetic constants. The ratio of alumina units possessing vacancies to those with none can be varied, which in turn determines the individual relative intensities of the resonances of the hole and electron which are observed simultaneously in the e.s.r. spectrum. The electrons produced by irradiation can be observed only if trapped by the vacancies; otherwise only the holes are observed.

Experimental

A. Sample Preparation.—The Linde type X and Y synthetic crystalline zeolites were used, having the compositions $Na_{86}[(AlO_2)_{86}(SiO_2)_{136}]$ and $Na_{88}[(AlO_2)_{88}(SiO_2)_{104}]$ of the unit cell, respectively.

The ammonium exchange samples were prepared by contacting the Na zeolite with an aqueous NH_4NO_3 solution, using the conventional ion-exchange technique. All the samples used for irradiation were degassed at 500° under vacuum ($\sim10^{-5}$) in a system free of stopcock grease. This thermal activation was carried out for at least 15 hr. The samples were then sealed under vacuum in quartz tubes (of 5 mm. o.d.). The samples in the quartz tubes were irradiated with a Co^{60} γ-source of about 4000 curies intensity. In all cases, except otherwise stated, a dose rate of approximately 1.9×10^7 roentgens was used. All samples were irradiated at room temperature. Before the e.s.r. measurements were performed, the powdered samples (about 1 in. length in the 5-mm. quartz tube) were kept in one end of the tube while immersed in an ice-water bath, while the other end was heated to 600° to obtain complete annealing. This treatment completely eliminates the e.s.r. found in the irradiated quartz tube. Then the powder was transferred to the annealed part of the tube and the e.s.r. spectra were obtained. This procedure proved to be more convenient than transferring the irradiated powders in a drybox from irradiated to nonirradiated tubes.

B. E.s.r. Measurements.—A Varian spectrometer (Model V4500) operating at 9.5 kMc./sec. and at TE_{102} mode was employed. The magnetic field was modulated at 100 kc./sec. and was measured by a proton magnetic resonance gauss meter. Varian conventional low temperature equipment was used. Low microwave powers were obtained with the Varian matching low power cavity. Spin concentrations were obtained by using a single crystal of $CuSO_4 \cdot 5H_2O$ with known susceptibility as a standard.

Results and Discussion

A. E.s.r. Absorption in the Irradiated NaX and NaY Zeolites.—A single e.s.r. line in both types of zeo-