

ESR Studies of Cationic Oxidation Sites in Faujasite

JAMES T. RICHARDSON

From the Esso Research and Engineering Co., Baytown Research and Development Division, Baytown, Texas

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ESR techniques have been used to measure the degree of ionization of anthracene, perylene, pyrene, and naphthalene by synthetic faujasite ion-exchanged with alkali, alkaline earth, and transition metal ions. It has been demonstrated that electron transfer occurs at the cation with the number of radical cations varying exponentially with the difference between the ionization energy of the hydrocarbon and the electron affinity of the cation. This electron affinity is drastically influenced by the polarizing effects of other cations, particularly those with lower affinities but larger ionic potentials. The relation of these oxidative sites with catalytic activity is discussed.

INTRODUCTION

It has been previously demonstrated that varying the exchangeable cation in zeolites drastically alters their catalytic properties (1-3). Current hypotheses explaining the nature of the active sites in near faujasites all invoke the role of these cations, either as the primary source of activity through electrostatic potential effects (2), as progressive poisons of some ultimate Lewis-Brønsted complex similar to those on amorphous surfaces (4), or as stabilizers for adjacent H⁺ sites (5). It is suggested that the cations initiate the catalytic reaction either through the acceptance of an electron to promote a radical-ion reaction or by perturbation of neighboring hydroxyl groups to yield Brønsted activity and associated carbonium ion activity. A series of experiments has been performed in this laboratory to investigate the relationship between predictable cation properties and the mechanism of acid catalysis. This paper describes the results of an electron spin resonance study on synthetic faujasite ion-exchanged with alkali, alkaline earth, and transition cations. ESR techniques have been used to follow the ionization of polynuclear aromatics and to correlate the oxidation effects with the

nature of the cation. The following papers will present the results of ESR studies on the zeolites themselves and of catalytic measurements on these materials.

EXPERIMENTAL

Preparation of samples. The starting material was a sample of synthetic sodium faujasite. Chemical and thermogravimetric analyses showed the composition to be Na₅₇(AlO₂)₅₇(SiO₂)₁₃₅·264 H₂O.

Conventional ion-exchange techniques were used under conditions yielding maximum exchange. The following series of samples were prepared in this manner:

- (1) Na faujasite at least 60% exchanged with K, Li, Ba, Sr, Ca, and Mg.
- (2) Na faujasite ion-exchanged with Ag and Cd.
- (3) Na faujasite ion-exchanged with Mn, Co, Ni, and Cu.
- (4) The samples of (1) above further exchanged with Cu to give approximately 2 wt % Cu or one Cu ion every two supercages.

ESR measurements. The ESR apparatus was a Strand Labs Inc. Model 600 EMR spectrometer modified with a Varian Associates V201B Klystron and V-4531 Cav-

ity, a 100-kc Field Modulation and Control Unit, and a Varian Model V-4012A 12-inch electromagnet. The instrument operated in the X-band at 9400 Mc/sec measured with a Hewlett Packard Co. Model X530A Frequency Meter. The magnetic field was measured and recorded using a Bell Inc. "240" Incremental Gaussmeter.

Solutions of perylene, anthracene, naphthalene, and pyrene were prepared in benzene at 10^{-2} molar concentration. The faujasite samples (100 mg in 4-mm tubes) were dehydrated by heating in air at 400°C for 12 hr. The tubes were sealed with serum caps and 150 μl of the appropriate solution injected. Experiments showed that spin equilibrium values were attained in 24 hr. The spin intensities were measured by comparing the radical cation ESR spectrum with that of a ruby secondary standard calibrated with DPPH. Appropriate corrections were made for variations in sample height within the various tubes.

RESULTS AND DISCUSSION

Polynuclear aromatics with low ionization potentials have been used to measure the relative ionizing ability of silica-

alumina catalysts and various zeolites (6-14). The mechanism for the formation of the radical cation has been pictured as either an electron transfer to a Lewis site (6-9), oxidation by molecular oxygen catalyzed by a Brönsted site (10-12), or an electron acceptance by the Brönsted site catalyzed by molecular oxygen (13). The zeolitic cage cations could initiate hydrocarbon ionization either directly through their electron affinity or by perturbation of the neighboring acceptor sites. The formation of radical cations from anthracene and similar aromatics is then an index of the electron-accepting or oxidation properties of the cage surface.

The ESR spectra of anthracene, naphthalene, perylene, and pyrene adsorbed on the ion-exchanged zeolites were characteristic of the appropriate positive radical ion (15). The results are given in Fig. 1, which shows the number of spins per cage cation versus the electron affinity of the cation. The electron affinities are the recombination energies deduced from the first or second ionization potentials of the elements (16). This practice is perhaps subject to question since the free ion ionization potential hardly represents the situation in the solid. Effects such as the

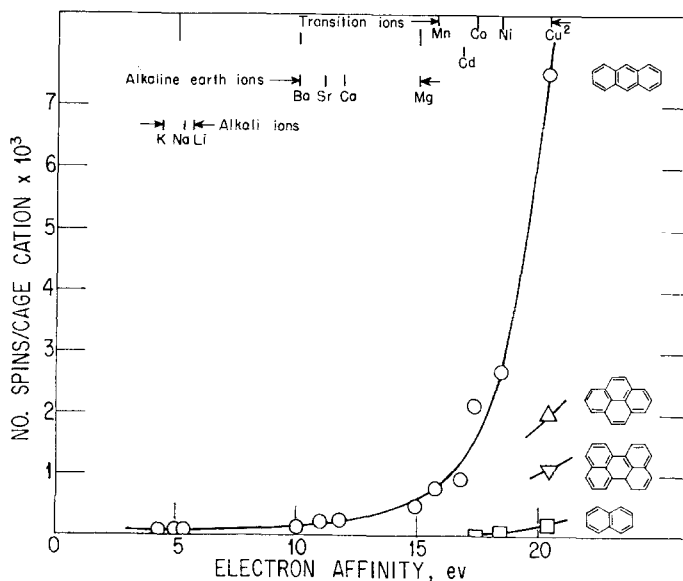


FIG. 1. Ionization of polynuclear aromatics versus electron affinity of cage cations.

Madelung potential and dielectric properties tend to lower ionization potentials. For example, the ionization potential of barium drops from the free ion value of 10 eV to 7 eV in BaO (17). Crystal field effects also enter into modification of the recombination energies of transition ions. The situation for surface ions is further complicated. Surface atoms of germanium have work functions of 4.8 eV compared to

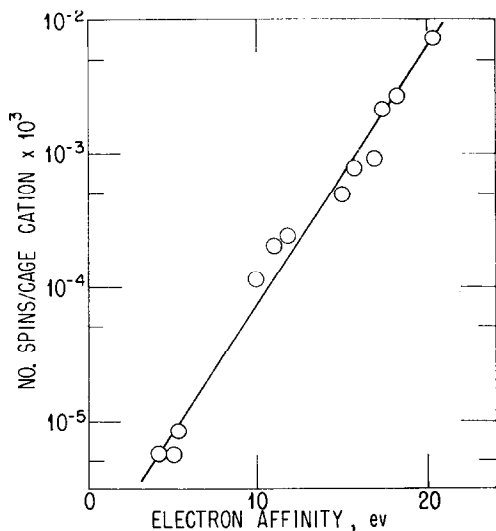


Fig. 2. Semilog plot of anthracene spins versus electron affinity.

16 eV for the free ion (18). There is no suitable method for predicting the ionization potential of surface atoms. In view of this, it is felt that use of the free ion ionization potentials in Fig. 1 is justified as an indication of the relative values for the various ions. It should be remembered that the actual values may be lower than those shown.

The results in Fig. 1 show a smooth variation of spin intensity with electron affinity. When the data for anthracene are plotted in Fig. 2 on a semilogarithmic scale, the variation is seen to be exponential. This is not surprising since the energy separation between the ground and excited states of a charge transfer complex may be given as (19)

$$E = I - A - W \quad (1)$$

where I is the ionization potential of the donor; A , the electron affinity of the acceptor; and W , the dissociation energy of the excited state. The number of cation radicals, N^+ , formed from N molecules is then

$$N^+ = N \exp(-(I - A - W)/kT) \quad (2)$$

which gives the observed dependence on A .

The final points for pyrene, perylene, and naphthalene are shown also in Fig. 1, the remaining points being omitted for clarity. The dependence of the spin concentration for the Cu sample on the ionization potential of the donor molecule is shown in Fig. 3. Naphthalene, pyrene, and

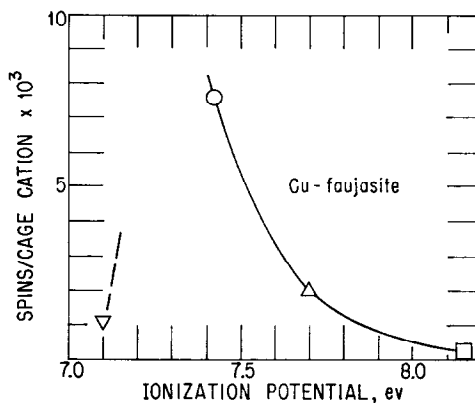


Fig. 3. Ionization versus ionization potential of hydrocarbon.

anthracene obey an exponential relationship as predicted by Eq. (2). However, perylene has a very low value. It should be noted that the diagonal dimensions of the perylene molecule are close to the super cage opening of the faujasite. Size effects are no doubt responsible for the decreased number of available perylene molecules inside the cages.

The direct role played by the cation is demonstrated in the following experiment: A number of samples of 2% Cu-Mg faujasite were dehydrated for 2 hr at temperatures from 100°C and the sample tubes sealed. Following the heat treatment, each sample was examined for the ESR spectrum of the Cu²⁺ ion and then treated with anthracene in the usual way. The anthracene spin intensity was subsequently

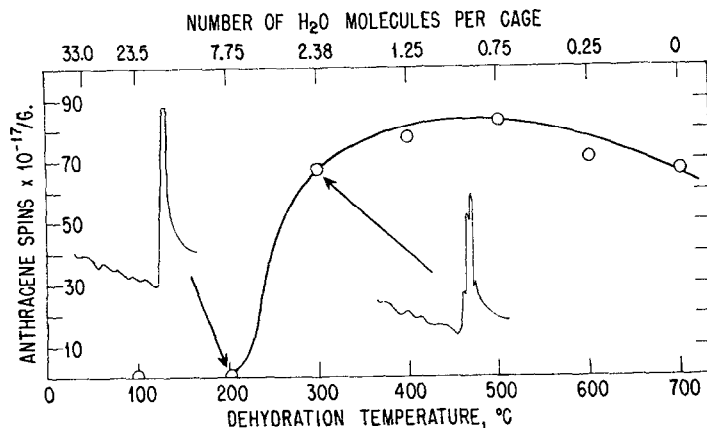


FIG. 4. Anthracene ionization versus temperature of dehydration.

measured. The same material was also treated in a similar manner on a quartz spring thermobalance so that the loss of water at each temperature was determined. The overall results are given in Fig. 4.

Up to a dehydration temperature of 200°C substantial amounts of water are lost but the ESR spectrum shows none of the high-field hyperfine structure characteristic of the dehydrated Cu^{2+} ion (20). There is no anthracene ionization at this temperature. At 300°C, however, the ESR spectrum shows that the Cu^{2+} ion is exposed. At the same time, electron transfer from the anthracene has taken place. This is an indication that the cation must be exposed before charge transfer occurs and that most likely the electron is accepted by the cation. Attempts to prove this last point through measurements of the Cu^{2+} peak intensities were unsuccessful since the total number of electrons transferred to the copper is too small to effect the overall signal.

The results above establish that electron transfer inside the cage involves the cation in the formation of the radical cation and that the driving force is the difference between the ionization potential of the molecule and the electron affinity of the cation, modified by the surface.

The results of the measurements on the samples of 2% Cu in exchanged faujasites are shown in Fig. 5. The ionization of the aromatics must be attributed to the effect of the copper since the samples without

copper give very much lower values. The effect demonstrated here is then a change in the ionization ability of the copper as the host cation changes from K^+ to Mg^{2+} . The results are reported on the basis of spin per copper ion. Since it was suspected that this effect of the cation was the result of changing ionic potential, the cationic parameter used is the polarizing power,

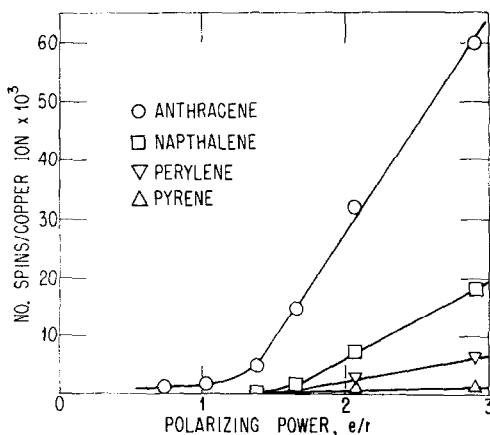


FIG. 5. Ionization versus polarizing power of main cage cation for Cu-containing faujasites.

e/r , the ionic charge divided by the ionic radius. The ionic potential of a cation at not too great distances may be shown to be related to e/r . This parameter is then a measure of the polarizing power of a cation in its immediate vicinity. Some authors (3) advocate e/r^2 but the effect is the same for the purposes here.

Figure 5 shows that increasing the polar-

izing power of the major cation increases the ionization of the aromatics by the copper. The effect is very pronounced, with the dependence on e/r also changing drastically as the valence of the cation goes from one to two. This suggests that factors other than direct ionic potential effects also enter into the process. It is interesting to compare the results of Fig. 5 with those of the copper sample in Fig. 1. Copper has a polarizing power of 2.85 so that the Cu^{2+} sample in Fig. 1 may be compared with the Mg^{2+} sample in Fig. 5. On a per gram basis, the Cu-Mg sample yields twice the number of anthracene spins as the Cu sample, or the ionizing potential of each Cu ion is increased by a factor of 8 by the combination with Mg^{2+} . The failure of Cu^{2+} ions to exert the same enhancement as Mg^{2+} on ionization by neighboring Cu^{2+} may be explained if Cu^{2+} actually has a lower effective polarizing power than Mg^{2+} . This would result from screening by ionized hydrocarbon molecules in the neighborhood of the Cu^{2+} ion. Since Cu^{2+} has a much larger electron affinity than Mg^{2+} , this "screening" effect would be more pronounced for the Cu^{2+} .

How does the cation exert its influence on the ionization by the Cu^{2+} ion? Does it alter the ionization potential of the hydrocarbon or the electron affinity of the Cu^{2+} ion? The problem of the energy levels of an aromatic in an electric field has not been treated theoretically. However, assuming that molecules behave like atoms, the theoretical quantum mechanical treatment of the polarized hydrogen atom shows that the energy levels are lowered (21). This would result in an increase of the ionization energy, which does not explain the observation.

The influence of the cations on the energy levels of the Cu^{2+} ions has been considered by the author in the following paper. Here it is shown that increasing the polarizing power of the cation results in an increase of the crystal field splitting of the Cu^{2+} ion in a square-planar complex with neighboring oxygen ions. This increased splitting would not result in an increase of electron affinity. On the

contrary, if this were the only result, the increased separation would mean an increase in the energy of the highest level of the d orbitals, thus a decrease in electron affinity. However, crystal field splitting effects result only from the spherically nonsymmetrical components of the electrostatic field. An increase in the symmetrical component would result in a lowering of all the levels; i.e., an increase in electron affinity as the polarizing power of neighboring ions is changed. There is no way to measure this change other than by the observations reported above.

CONCLUSIONS

The above experiments provide a clear picture of the role of zeolitic cations in the ionization of hydrocarbons to form radical cations. It has been demonstrated that the electron transfer occurs at the cation and that the degree of ionization is related to the difference between the ionization energy of the hydrocarbon and the electron affinity of the cation. This latter parameter is modified by the surface effects but is also drastically influenced by the polarizing effect of other cations. The effect is particularly great when a cation of high electron affinity is polarized by other cations with large polarizing powers but lower affinities. Cation polarization effects seem to predominate over hydrocarbon polarization in promoting the mechanism. This does not, however, diminish the role of cationic electrostatic fields in the formation of pseudocarbonium ions but rather emphasizes the large differences of electrostatic field strengths resulting from different cations within the cages.

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