

The Generation of Free Radicals by Cerium-Exchanged Zeolites

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Received July 1, 1970

Electron spin resonance and bulk magnetic susceptibility techniques were used to study the radigenic activity of cerium-exchanged zeolites. It was shown that the high radigenic activity of cerium-exchanged zeolites as compared to other lanthanide-exchanged zeolites is due to the presence of Ce^{4+} which is formed during activation in the presence of oxygen. The radigenic sites associated with Ce^{4+} have rather discrete energies; the bulk of these are of such energy that they can oxidize molecules of ionization potential 7.5 V and less. A lesser number of sites are present which can oxidize molecules with ionization potentials up to circa 9.0 V. These higher energy sites are associated with sodalite cages containing two cerium ions. The 7.5 V site is not situated within zeolite supercages but exists on the exterior surface of zeolite crystallites.

INTRODUCTION

The application of ESR techniques to the study of the generation of free radicals on zeolites (1-4) has not shown the location of the active sites nor has the role of cations in the zeolite been clearly defined. For instance, in the pioneering studies of Stamires and Turkevich (1) on decationized zeolites, it was concluded that active sites existed in the interior of zeolite supercages. In spite of the fact that adsorption occurred to the extent of one molecule per supercage, only one molecule in twenty was oxidized to a free radical. It was necessary to postulate rather bizarre schemes to explain the reduced reactivity of the test molecule. Richardson (3) has concluded that the electron acceptor in Cu^{2+} exchanged zeolites is the Cu^{2+} ion. The basis for this conclusion is the appearance of Cu^{2+} hyperfine splitting at the same activation temperature as is necessary for the production of a radigenic catalyst. It is plausible, but not proven, that the cation is the electron acceptor.

In this paper, we report the results of experiments using ESR and bulk magnetic susceptibility techniques which bear on these problems for cerium-exchanged zeo-

lites. Evidence is presented which suggests that indeed the active sites are not located in the interior of the zeolite, but exist on the exterior surface of the zeolite. Further, it is shown that during activation, Ce^{3+} is oxidized to Ce^{4+} and that Ce^{4+} is closely associated with the active site. No direct evidence was obtained which would rule out reduction of Ce^{4+} by adsorbed hydrocarbon, but it is postulated that the role of Ce^{4+} is to enhance the radigenic activity of surface sites associated with conventional Lewis or Brönsted acids.

EXPERIMENTAL

ESR Measurements

A conventional Varian V-4502 EPR spectrometer with 100 kHz field modulation was used in these experiments. Spin counting was done using the Varian V-4531 dual cavity with benzene solutions of DPPH as standards. These DPPH solutions were periodically compared to Varian's standard pitch samples in order to verify the number of spins. Integration of the first derivative signal was accomplished via a numerical first moment analysis as outlined by Ayscough (10). The measure-

ment interval was chosen so that as many as 100 products $xf(x)$ were obtained on a single curve. Care was taken to insure that we always worked at power levels on the ascending portion of the signal intensity versus power curve. In general, 10 mg zeolite samples were used. These samples were treated with solutions of the hydrocarbon in CCl_4 until no further increase in signal intensity occurred with addition of fresh solution. The samples were placed in the cavity at the position of maximum signal intensity. The signal intensity was found to fall off if samples were placed above or below the center of the cavity. When the volume of zeolite was kept low (i.e., a 10-mg sample was used), the signal intensity was found (by experiments conducted with DPPH solutions) to be a true representation of the number of free radicals in the cavity.

Sample Preparation

The zeolites used in this study were prepared by ion exchange of the sodium Y zeolite with NH_4Cl followed by exchange with the appropriate lanthanide salt. Samples for ESR examination were prepared by weighing 10 mg of zeolite into an ESR

tube and subsequent addition of CCl_4 solutions of the appropriate hydrocarbon. No appreciable difference in signal intensity was noted when samples were prepared from degassed CCl_4 solutions added under vacuum to catalysts freshly activated at 500°C in air or oxygen so that the simpler procedure described above was routinely used.

Magnetic Susceptibility Measurements

Measurement of the bulk susceptibility was made using a quartz helix spring and a measuring microscope in the manner described by Senftle *et al.* (5). The reproducibility was often better than the 2% suggested by Senftle but the accuracy was often near 20% for strongly paramagnetic samples. For diamagnetic samples the accuracy was excellent. The apparatus of Senftle is such that activation within it is possible and weight changes upon activation can be measured directly. Sodium chloride, potassium chloride, and sucrose were used as standards. Samples of platinum, palladium, and nickel chloride experience severe horizontal displacement in the magnetic field and thus give erratic results. With the cerium-exchanged zeolite

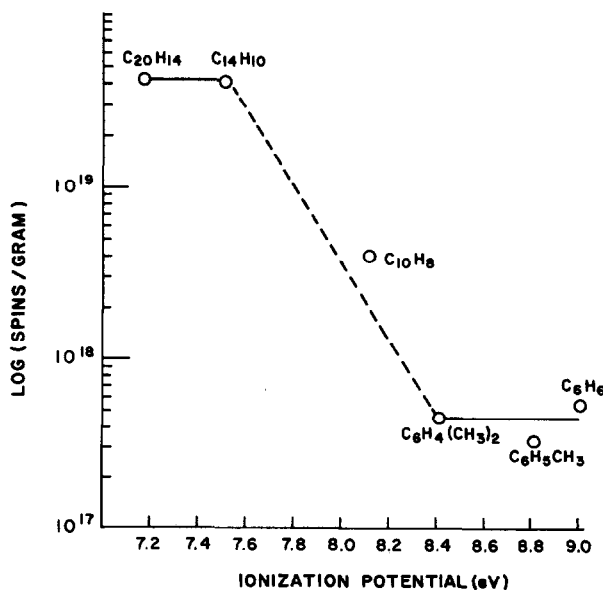


FIG. 1. Variation of spins generated on a 13.3% cerium-exchanged zeolite with the ionization potential of the adsorbed molecule.

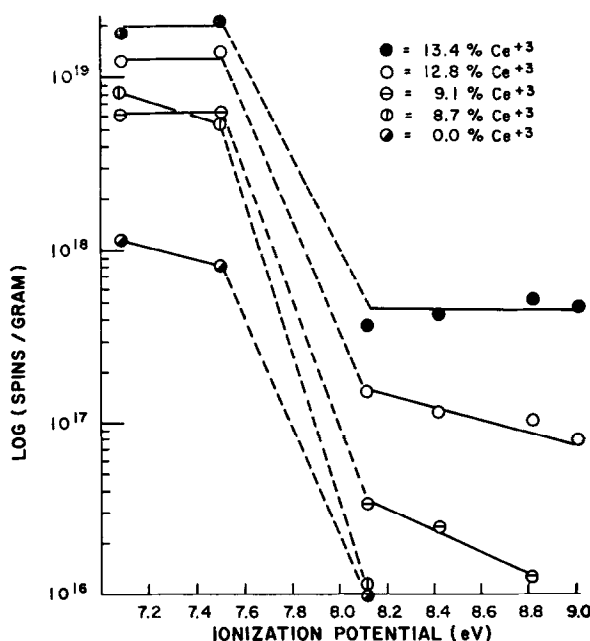


FIG. 2. Variation of spins generated with the ionization potential of the adsorbed molecule.

no horizontal displacement was observed when the amount of sample was kept below 5 mg and thus it is thought that these results are rather reliable.

RESULTS

Figure 1 shows a plot of the number of free radicals detected versus the ionization potential of the adsorbed molecule for the adsorption of benzene, toluene, *p*-xylene, naphthalene, anthracene and perylene on cerium (13.3%)-exchanged Y zeolite. The data were obtained by adsorbing the individual hydrocarbon from CCl_4 solution onto a fresh sample of zeolite for each point. A similar plot is shown in Fig. 2 for zeolites of varying cerium content. The results shown in Fig. 2, however, were obtained by successively adding the various hydrocarbons in order of decreasing ionization potential to a single zeolite sample. The curves obtained in Figs. 1 and 2 are not obviously linear, as was predicted by Richardson (3), but consist more nearly of two essentially flat regions connected by a transition region in the vicinity of the ionization potential of naphthalene. It is clear from comparing the 13.3% cerium

curve of Fig. 2 with the curve of Fig. 1 that adsorption of the hydrocarbons benzene, toluene, *p*-xylene, and naphthalene onto the zeolite prior to adsorption of anthracene has only a slight effect on the zeolite's ability to generate free radicals from anthracene. Note, however, that the naphthalene point is much lower in Fig. 2 than in Fig. 1. Reaction apparently occurs between the naphthalene positive ion radical and other adsorbed hydrocarbons. The adsorption of anthracene, however, in Fig. 2 results in complete utilization of the remaining sites so that essentially no additional free radicals are generated by the adsorption of perylene.

Table 1 compares the total number of molecules adsorbed per gram of zeolite for anthracene, perylene and coronene with the number of free radicals formed per gram of zeolite when these molecules were adsorbed. In Table 1 the number of molecules adsorbed was computed from the loss of aromatic hydrocarbon in the liquid phase during contact with the zeolite as determined gravimetrically. A sample of the liquid phase was withdrawn from contact with the zeolite and the CCl_4 solvent

TABLE 1
COMPARISON BETWEEN THE NUMBER OF SPINS
GENERATED PER GRAM ON A SIEVE OF 13.3%
CERIUM CONTENT AND THE TOTAL
NUMBER OF MOLECULES
ADSORBED PER GRAM

No. molecules adsorbed/g	No. spins/g	Ratio
		No. spins/ No. mole- cules adsorbed
Anthracene, 5.05×10^{20}	4.17×10^{19}	1:12
Perylene, 4.37×10^{19}	4.34×10^{19}	1:1
Coronene, 1.63×10^{19}	6.8×10^{17}	1:11.4

removed by passing a stream of N_2 over the surface and the residue weighed. The results obtained in this way for anthracene were in agreement with those obtained from analysis of the uv spectra. For coronene and perylene, the simpler gravimetric procedure was used. The data presented in Fig. 3 show the time dependence of spin generation and adsorption of anthracene. Within the first hour after contact of the anthracene solution with the catalyst, there is a one to one correspondence between molecules adsorbed and spins generated. At the end of an hour spin generation is essentially complete, yet anthracene ad-

TABLE 2
COMPARISON BETWEEN THE CALCULATED SURFACE
CERIUM IONS AND THE NUMBER OF
ANTHRACENE SPINS DETECTED

Wt % Ce	Ce_{tot}/g	Ce_{calcd} at surface/ g^a	Anthracene spins/g
0.0	—	—	1.2×10^{18}
4.02	1.73×10^{20}	9.13×10^{18}	8.9×10^{18}
8.0	3.44×10^{20}	1.82×10^{19}	1.19×10^{19}
11.3	4.86×10^{20}	2.57×10^{19}	2.35×10^{19}
13.3	5.72×10^{20}	3.02×10^{19}	4.17×10^{19}
Average		2.08×10^{19}	2.15×10^{19}

^a Calculated using model of Uytterhoeven *et al.* (8).

sorption continues for at least 22 hr, finally reaching a value, in this experiment, of about 21 times the number of spins generated. The time interval in Fig. 3 between zero and the first point on the spin curve was governed by the rate of settling of catalyst in the ESR tubes after mixing so that it is possible that spin generation is complete in some shorter time than indicated. When perylene was the adsorbate maximum spins were generated in the first few minutes as well.

In Table 2 a comparison is shown between the number of ion radicals formed from anthracene on zeolites of five different cerium contents and the number of cerium

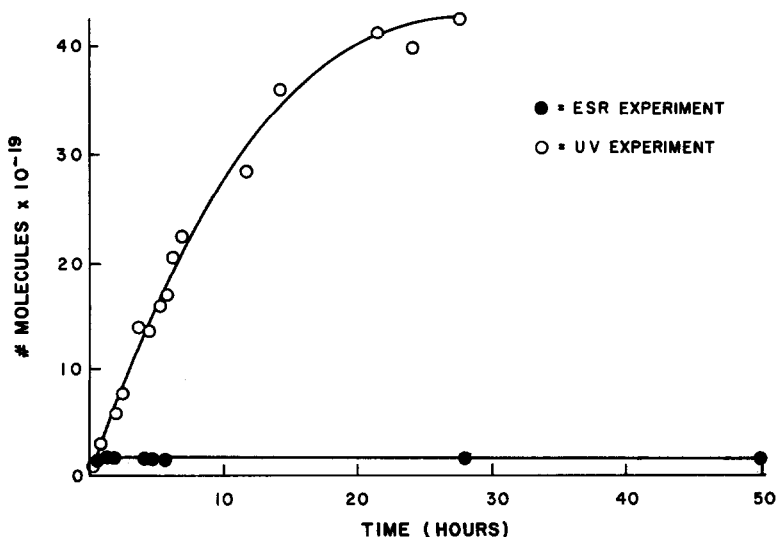


FIG. 3. Comparison of anthracene spins generated with total anthracene adsorbed, on cerium-exchanged zeolite.

TABLE 3
THE EFFECT OF RARE EARTH COUNTER IONS ON
THE RADIGENIC NATURE OF EXCHANGED
ZEOLITES

Exchange material	Wt % rare earth in zeolite	Anthracene spins generated/g-catalyst
LaCl ₃	11.00	4.15 × 10 ¹⁸
La(NO ₃) ₃	13.00	3.07 × 10 ¹⁸
Ce(NO ₃) ₃	13.30	3.36 × 10 ¹⁹
CeCl ₃	12.93	1.87 × 10 ¹⁹
Ce ₂ (SO ₄) ₃	12.85	8.3 × 10 ¹⁸
SmCl ₃	14.86	4.76 × 10 ¹⁸
Sm(NO ₃) ₃	13.27	4.46 × 10 ¹⁸
Gd(NO ₃) ₃	14.39	0 (<10 ¹⁶)
GdCl ₃	13.33	0 (<10 ¹⁶)
DyCl ₃	14.22	3.18 × 10 ¹⁸

ions estimated to exist near the exterior surface of the zeolite. Also listed for comparison purposes is the total number of cerium ions per g-catalyst. The number of cerium ions on the exterior surface was estimated from the average crystallite size (1450 Å) using a modification of the model developed by Uytterhoven, Christner, and Hall (8) for estimating surface hydroxyl groups. Table 3 lists the number of anthracene spins generated on Y zeolite exchanged with various lanthanide salts. Of the catalysts studied, cerium exchange clearly produces the most radigenically active catalyst. No spins could be detected when gadolinium was the counter ion. Table 4 compares the number of spins generated from anthracene for activation at 500°C in air, hydrogen and helium. Clearly oxygen is necessary for the production of an active catalyst.

Table 5 compares the magnetic susceptibility of a cerium-exchanged zeolite with that from a sodium-exchanged zeolite be-

TABLE 4
THE NUMBER OF FREE RADICALS GENERATED FROM
ZEOLITES ACTIVATED IN AIR, HELIUM AND
HYDROGEN

Wt % Ce	Activation atmosphere, 500°C	Anthracene spins/g
13.3	Air	1.16 × 10 ¹⁹
13.3	Helium	7.2 × 10 ¹⁷
13.3	Hydrogen	9.00 × 10 ¹⁷
0.0	Air	1.2 × 10 ¹⁸
0.0	Hydrogen	1.03 × 10 ¹⁶

fore and after activation in the presence of oxygen at 500°C. As expected, the unactivated Ce³⁺-exchanged zeolite is paramagnetic; activation, however, considerably decreases the susceptibility. The sample of NaY shown was diamagnetic before and after activation. In Table 6, we summarize the change observed in the susceptibility of a cerium-exchanged zeolite for various activation conditions. Activation in a helium atmosphere does not result in a significant change in susceptibility. Contact of the helium activated sample with oxygen at atmospheric pressure for 16 hr produced only a slight increase in susceptibility. This increase may be due to adsorption of paramagnetic oxygen. Activation of this helium-oxygen treated sample in the presence of oxygen at 500°C resulted in a reduction in susceptibility to about half the unactivated value.

Figure 4 shows a plot of the number of anthracene free radicals generated on a cerium-exchanged zeolite versus the temperature of activation of the catalyst. The number of free radicals generated increases up to 700°C according to the equation.

$$\log(\# \text{ spins}) = 3.33 \times 10^{-3} T^{\circ}\text{C} + 17.65.$$

TABLE 5
THE CHANGE IN MAGNETIC SUSCEPTIBILITY UPON ACTIVATION IN OXYGEN AT 500°C

Sample	Weight (mg)	χ/g unactivated	Weight after activation	Wt % loss	χ/g activated
CeY	4.3	1.24 × 10 ⁻⁶	3.39	21.0	0.38 × 10 ⁻⁶
CeY	3.5	1.09 × 10 ⁻⁶	2.70	22.8	0.16 × 10 ⁻⁶
CeY	—	—	2.90	—	0.21 × 10 ⁻⁶
NaY	7.6	-0.155 × 10 ⁻⁶	5.80	24.0	-0.095 × 10 ⁻⁶

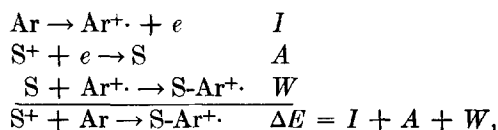
Above 700°C there is a sharp decrease in the radigenic activity of the catalyst which is probably due to collapse of the zeolite crystal structure. Table 7 shows the change in bulk susceptibility of cerium-exchanged catalysts for several activation temperatures. Also shown in Table 7 are the number of anthracene free radicals found for catalysts activated at the temperatures listed and the number of Ce⁴⁺ ions at the catalyst surface estimated from the reduction in susceptibility and the total number of cerium ions thought to be present on the surface as given in Table 2.

DISCUSSION

Richardson (3) has interpreted plots of numbers of spins versus the ionization potential of adsorbed molecules in terms of a Boltzman distribution.

$$N^+ = N_0 e^{-\Delta E/kT},$$

where ΔE is the sum of the ionization potential of the adsorbed molecule, the electron affinity of the surface and the charge transfer energy. These processes are illustrated in the following scheme:



where S and Ar represent the surface and aromatic hydrocarbon, respectively.

This equation predicts that plots of the logarithm of the number of free radicals generated versus the ionization potential of the adsorbed molecule will be a straight

TABLE 6
VARIATION OF MAGNETIC SUSCEPTIBILITY WITH CHANGE OF ACTIVATION ATMOSPHERE AT 500°C FOR 13.3% CERIUM ZEOLITE

Activation atmosphere	$\chi \times 10^6$	$\chi M\text{Ce} \times 10^6$
Unactivated sample	1.63	32,590 ^{a,b}
Helium	2.17	31,010 ^a
Helium O ₂ contact for 16 hr after activation	2.44	34,710 ^a
Oxygen	1.06	16,760 ^a

^a Value obtained by correcting for silica-alumina network.

^b Corrected for loss of water.

line when variations of A and W are small. The curves shown in Figs. 1 and 2 however are not exponential but appear to consist of two essentially constant regions of spin separated by a transitional region. It seems that these curves are better interpreted to mean that sites of rather discrete potential energy exist on the zeolite. Considering the 13.3% cerium sample used in obtaining the data shown in Fig. 1, the plot can be interpreted to mean that sites of rather discrete potential energy exist on the zeolite. In Fig. 1, there are 4×10^{17} sites of sufficient energy to oxidize molecules whose ionization potentials are less than 9.0 V and 4×10^{19} sites capable of ionizing molecules whose ionization potentials are 7.5 V or less. There is a third site of intermediate energy near 8.2 V; however, its limits were not clearly defined. It is clear using this view of the surface why identical numbers of free radicals are obtained from benzene, toluene, and *p*-xylene. These molecules

TABLE 7
VARIATION IN MAGNETIC SUSCEPTIBILITY WITH ACTIVATION TEMPERATURE FOR A 13.3% CERIUM ZEOLITE

Activation temp (°C)	$\chi M\text{Ce} \times 10^6$	$\Delta\chi M\text{Ce} \times 10^{18}$ ^a	No. of Ce ⁴⁺ at surface/g ^b	No. anthracene spins/g
Unactivated	28,590	—	—	—
210	29,810	+1,230	—	2.14×10^{18}
305	24,010	-4,580	4.80×10^{18}	4.66×10^{18}
405	17,910	-10,680	11.22×10^{18}	8.2×10^{18}
505	11,010	-17,580	1.85×10^{19}	2.2×10^{19}
Average			1.15×10^{19}	1.16×10^{19}

^a $\chi M\text{Ce} - 28,590$.

^b See text.

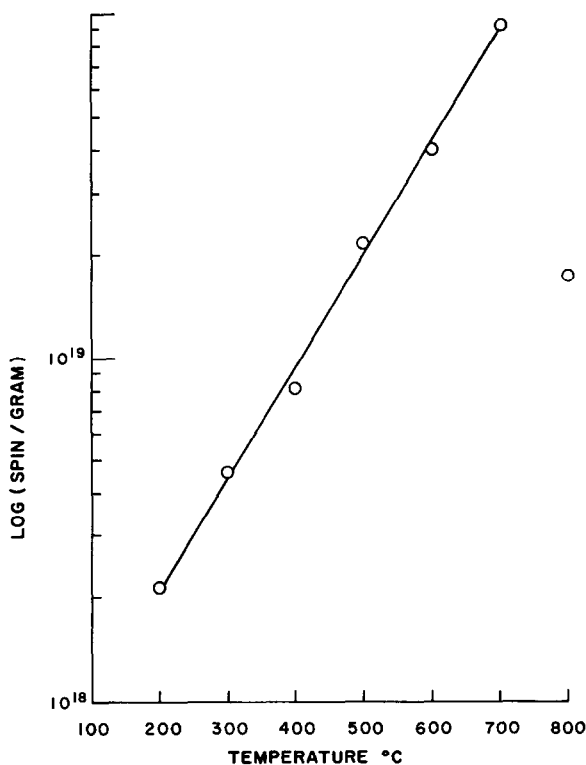


FIG. 4. Variation of anthracene spins generated with activation temperature of the zeolite.

cannot be ionized by the low energy sites (7.5-V sites), they can react only with the 9.0-V sites. The number of radical ions generated is not governed by a Boltzman distribution. Similarly the equal numbers of perylene and anthracene radicals can be explained, i.e., they both react at the 7.5-V site with complete utilization of the available sites. The plots shown in Fig. 2 strengthen this hypothesis. From an examination of Fig. 2 it can be seen that adsorption of benzene, toluene, xylene, or naphthalene onto the zeolite does not appreciably affect the radical nature of the surface towards anthracene or perylene, i.e., molecules whose ionization potentials exceed ca. 8.1 V cannot react at the 7.5-V sites. It is also evident from the figure that the number of these sites depends heavily on the cerium content of the zeolite. A reduction in cerium content from 13.4 to 8.7% reduces the number of 7.5-V sites by a factor of 4 while the number of 9.0-V sites is reduced by about a factor of 50. For catalysts with

a cerium content 8.7% and less, no ESR signal could be detected for adsorption of molecules of higher ionization potential than naphthalene. This observation implies that the 9.0-V site results from the pairing of cerium ions in the more strongly exchanged zeolites. Olson, Kokotailo, and Charnell (7) have estimated that the sodalite cages contain 1.56 cerium atoms after activation with the arrangement two cerium atoms per cage in one-half of the cages and one cerium atom per cage in the other half. Appreciable pairing probably does not occur until the exchange approaches 10.4% cerium which is consistent with the rapid decrease in number of spins observed for zeolites of lower cerium content at the 9-V site. It should be noted that 8.7% cerium-exchanged zeolite is indistinguishable from decationized Y as regards reaction with naphthalene. This is consistent with the explanation for the 9-V site, viz., that it results from pairing of cerium atoms in the sodalite cage.

Information can be inferred about the

nature of the 7.5-V sites by referring to the data of Table 1. The lower number of perylene and coronene molecules adsorbed onto the zeolite as compared to anthracene suggests that these molecules do not enter the supercage of the zeolite. Indeed this is expected from a consideration of the sizes of these molecules as compared to the diameter of the window of the supercage. The shortest diameter for perylene and coronene are approximately 7.7 and 10.4 Å, respectively, as compared to a short diameter of approximately 6 Å for anthracene (11) and a supercage window diameter of about 7.5 Å (7). Accordingly, radical ions resulting from perylene and coronene must result from reaction with sites situated at the external surface of zeolite crystallites. There is a one to one correspondence in Table 1 between perylene molecules adsorbed and spins generated. With anthracene, however, the interior cavities of the zeolite should be accessible and indeed there is roughly 12 times as much anthracene adsorbed as perylene. Since the number of free radicals formed from anthracene is identical to the number formed from perylene, the sites must be identical and are not situated in the cavity interior as has been supposed previously (1), but are on the exterior surface of the zeolite crystallites. This conclusion is supported by the data presented in Fig. 3. Within the first hour after contact of the anthracene solution with the catalyst there is a one-to-one correspondence between molecules adsorbed and spins generated. At the end of an hour spin, generation is essentially complete yet anthracene adsorption continues for at least 22 hr finally reaching a value in this experiment of about 21 times the number of spins generated. Initial adsorption of anthracene would be expected to occur on the exterior surface of zeolite crystallites with further adsorption into the interior of the crystallites, by way of the supercage windows, requiring longer times. Thus the rapid completion of spin generation is consistent with the suggestion that radigenic sites exist only on the exterior crystallite surface. With perylene the spin generation curve is identical with the adsorption curve. When anthracene

was ground with dry catalyst in a mortar, nearly the same number of spins were obtained as when adsorption occurred from solution although spin counts were not made due to rapid deterioration of the signal. In Stamire's and Turkevitch's studies of decationized zeolites a severe limitation of their theory was the fact that with triphenylamine twenty times as much material was adsorbed as spins detected. It seems likely that the active sites in that system are on the exterior surface as well. This suggestion substantiated somewhat by the data shown in Fig. 2 where essentially identical numbers of perylene and anthracene spins were obtained over a decationized zeolite. The adsorption characteristics of the decationized zeolite would not be expected to differ significantly from those of the cerium-exchanged material as regards the adsorption of perylene and anthracene. The lower number of coronene ion radicals detected suggests that even on the exterior surface the size of the molecule is an important factor in determining reaction at a radigenic site.

The location of the 9-V sites is less clear. If they lie deep within the zeolite, reaction first with perylene would not deactivate them and subsequent reaction with benzene would increase the number of spins generated. Spin counting is not sufficiently reproducible, however, to permit detection of an additional 10^{18} spins when 10^{19} are already present. A study of spin growth as a function of time might illuminate this problem. Preliminary experiments in this direction have been made utilizing the adsorption of benzene on the zeolite. With benzene spin growth was observed for 20 hr following contact of the catalyst with a benzene solution which suggests that these sites may indeed lie deep within the crystallite. These sites, as was indicated earlier, probably are associated with the presence of two cerium ions in the sodalite cages.

The conclusion that radigenic sites in the main exist at the external surface is strengthened by the data in Table 2. Here the number of cerium ions estimated to exist near the exterior surface is compared with the number of spins detected. There

is, considering the inaccuracies inherent in spin counting and the model used for the zeolite, excellent correspondence between these two sets of numbers. For the four catalysts studied the average number of cerium ions at the surface per gram of catalyst is 2.08×10^{19} while the average number of ion radicals found is 2.15×10^{19} . It should be noted that the total number of cerium ions in the zeolite is 20 times greater than these numbers.

The number of cerium ions at the exterior surface was estimated from a modification of the model suggested by Uytterhoeven, Christner, and Hall (8) for the calculation of surface hydroxyl groups. Faujasite is made up of sodalite cages (cubo-octahedra) joined by hexagonal faces on the cubo-octahedra to four tetrahedrally situated neighbors. If N is the number of cubo-octahedra per crystallite then there are $4N$ hexagonal faces which can join to neighboring cubo-octahedra. Each time a juncture (J) between cubo-octahedra is formed, two hexagonal faces are used up, i.e., the number of unused hexagonal faces per crystallite (i.e., the number on the surface) is $K = 4N - 2J$. The ratio K/N will give the number of unterminated faces per cubo-octahedron.

$$\frac{K}{N} = 2 \left(2 - \frac{J}{N} \right).$$

The zeolite in this model is made of sheets of cubo-octahedra arranged in a hexagonal array; there are h hexagons per sheet edge and h sheets per crystallite. Using the UCH values of N and J yields a value of $K = 8h^2$. The edge size X was related to h and the lattice constant a_0 by $X = a_0 / \sqrt{2h}$ giving $K = 16(X/a_0)^2$. The edge size was estimated, from line broadening in the X-ray diffraction pattern, as 1450 Å. The number of crystallites per gram was estimated to be $(N_0/M)(a_0/X)$, where N_0 is Avagadro's number and M is the molecular weight of the zeolite. K per gram then follows as

$$K/g = 16 \left(\frac{X}{a_0} \right) \left(\frac{N_0}{M} \right) = 1.19 \times 10^{19}.$$

This number represents the number of unshared hexagonal faces on the cubo-octahedra per gram of zeolite. For purposes of counting cerium ions we are interested in the total number of cubo-octahedra which is twice the unterminated number, viz., 2.38×10^{19} . There are four S-II sites per cubo-octahedron but only 36% are occupied in the cerium-exchanged zeolite (7), therefore, the number of cerium ions is 3.71×10^{19} for a completely exchanged zeolite. This number was scaled downwards to account for incomplete exchange in our samples. The agreement between these calculated numbers and experiment in Table 2 is excellent; it should be realized that such good agreement is really fortuitous. The UCH model treats the faujasite crystallites as rhombohedra whereas they are probably octahedra. Kerr, Dempsey, and Mikovsky (9) have developed an octahedral model of faujasite which would lower the number of surface cerium ions to one-half that used here. In addition, the estimation of crystallite size from X-ray line broadening is subject to large errors and the edge size might be in error by 50%.

Of the five lanthanide-exchanged catalysts listed in Table 3 the cerium-exchanged catalyst is clearly the most radically active. With gadolinium-exchanged zeolite no spins were detected. This is particularly puzzling considering the behavior of the other rare earth ions and the rather pronounced radigenic behavior of the decaionized zeolite.

In view of the signal observed with the strongly paramagnetic dysprosium exchanged material it does not seem possible to attribute this negative result to line broadening of the resonance signals by the gadolinium ion. The strong coloration characteristic of the aromatic ion radicals is absent when aromatic hydrocarbons are added to the gadolinium exchanged zeolite and thus on this visual observation alone it seems evident that ion radicals are not present. The fact that identical results were obtained with two different exchange materials would seem to rule out an artifact of the exchange process as an explanation. Indeed the gadolinium-exchanged ma-

terial functions in much the same way as other rare-earth-exchanged zeolites in catalytic test reactions. We can find no explanation for this result in the known chemistry of the lanthanides and prefer not to speculate without further experimental work.

It has been suggested (12) that Ce^{4+} might be responsible for the unique properties of cerium-exchanged zeolites. Of those lanthanides studied here only cerium has a stable $4+$ oxidation state. The supposition that Ce^{4+} is involved in the active site is particularly satisfying as it provides the strong oxidizing character necessary to explain the ionization of olefins and benzene (4) by these zeolites. Additional evidence in support of this hypothesis is given in Table 4 where it is shown that activation in the presence of oxygen is necessary to produce a catalyst of high radigenic ability.

Cerium in the plus three oxidation state has one $4f$ electron and consequently Ce^{3+} is paramagnetic. Oxidation of Ce^{3+} to Ce^{4+} results in the loss of this electron and a change from paramagnetic to diamagnetic.

Initial attempts to measure the magnetic susceptibility of activated zeolites failed due to the presence of iron impurities which upon activation were converted to Fe_2O_3 which is ferromagnetic (6). Essentially iron free samples of NaY zeolite were obtained by special request from the Union Carbide Corp. Activation of these unexchanged NaY samples resulted in only a slight increase in susceptibility so they are essentially free of interfering impurities. A further check on the purity of these zeolites was made by observing the ESR spectrum after activation. Neither the NaY or the final cerium exchanged material showed the typical ESR spectrum of Fe^{3+} . Table V shows the specific susceptibility of NaY and cerium-exchanged zeolites before and after activation. The susceptibility per gram decreases for the cerium-exchanged zeolite from an average value of 1.17×10^{-6} before activation to 0.25×10^{-6} after activation. From the weight loss upon activation, the molecular formula for the unactivated 13.3% exchanged zeo-

lite is estimated to be $Ce_{13}H_{17}(AlO_2)_{56}(SiO_2)_{136} \cdot 213H_2O$ which has a molecular weight of 17,124. This number is slightly in error since all the water has not been removed during activation. The molar susceptibility of unactivated cerium-exchanged zeolite is therefore $20,025 \times 10^{-6}$. The susceptibility value for NaY may be used with only slight error to correct for the silica-alumina network of the zeolite. Subtracting the contributions of water and the silica-alumina framework from the molar susceptibility of unactivated zeolite the value $\chi M_{Ce} = 23,015 \times 10^{-6}$ is obtained. This is the molar susceptibility for cerium before activation. In order to compare this number with the atomic susceptibility χ_A of cerium it must be divided by thirteen; the number of times cerium appears in the molecular formula. This gives a value for the atomic susceptibility of 1.770×10^{-6} which is 35% lower than the theoretical value for cerium viz. $2,750 \times 10^{-6}$ (14). The agreement with other experimental values (13, 14) is much better however and is generally within the 20% error quoted previously for this method. After activation it is only necessary to correct for the susceptibility of the silica-alumina network, neglecting the slight contribution of residual water to the susceptibility. The molar susceptibility after activation is $3,403 \times 10^{-6}$. Correcting for the silica-alumina network yields $\chi M_{Ce} \text{ act.} = 4,613 \times 10^{-6}$. Assuming that the change in susceptibility represents the disappearance of Ce^{3+} and the appearance Ce^{4+} the fraction of Ce^{3+} that has disappeared is thus $18,402/25,015 = 0.80$. Thus 80% of the cerium originally present as Ce^{3+} has been converted to Ce^{4+} by activation in oxygen at $500^\circ C$.

Reduction of the average value of cerium ions estimated to exist on the surface (Table 2) by 20% gives the average number of Ce^{4+} ions as 1.66×10^{19} which is still in agreement with the average number of spins observed, viz., 2.15×10^{19} .

Table 6 shows the effect on the susceptibility of activation in the presence of helium, contact of helium activated catalyst with oxygen at ambient temperature, and finally of activation in oxygen. There

is very little change between activated and unactivated catalyst when helium is the activation atmosphere and thus little or no Ce^{4+} is produced. When the catalyst was exposed to oxygen at atmospheric pressure for 16 hr, only a slight increase in magnetic susceptibility was noted; this was presumably due to oxygen adsorption by the zeolite. The important point, however, is that there is no indication of significant Ce^{4+} production during these procedures. In this regard, exposure of helium or vacuum activated catalyst to oxygen at room temperature increases their radiogenic activity about fourfold. This increase is probably not due to Ce^{4+} production but rather to the enhancement of the activity of surface sites already present by adsorbed oxygen (15). Dollish and Hall (2) have suggested that this increase is due to the formation of ion pairs ($Ar^+O_2^-$) between adsorbed oxygen and aromatic hydrocarbon (Ar); the data reported here cannot be used to distinguish between these suggestions.

Figure 4 shows a plot of the number of anthracene spins generated versus the temperature at which the catalyst was activated in air. Table 7 shows the variation of susceptibility as the activation temperature is increased. Indeed the susceptibility drops as the temperature of activation is increased, indicating that the conversion of Ce^{3+} to Ce^{4+} is favored by higher activation temperatures. The number of cerium atoms on the surface was previously estimated as 3.02×10^{19} per gram for the 13.3% exchanged zeolite. The number of Ce^{4+} ions formed at the surface during activation may be estimated by multiplying 3.02×10^{19} by the fractional change in susceptibility during activation. This number and the number of anthracene spins per gram are listed in Table 7 as well. The estimated number of Ce^{4+} ions on the surface agrees quite well with the number of spins generated when anthracene is adsorbed.

The fate of the Ce^{4+} ions after reaction of the zeolite with aromatic hydrocarbons is not clear. Richardson (3) has claimed that copper exchanged zeolites experience a

reduction of the copper ion upon reaction with aromatic hydrocarbon. Another equally plausible hypothesis is that the presence of the Ce^{4+} ion serves to increase the electron affinity of surface sites associated with Lewis or Brönsted acids without actually becoming an electron acceptor.

ACKNOWLEDGMENT

The assistance of Mr. R. L. James and Mr. R. E. Ledy III who carried out much of the experimental work for this paper, Mr. W. P. Griffin who offered helpful suggestions during the course of this research and Dr. M. A. Vannice who made constructive comments during the preparation of the manuscript is appreciated by the author.

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