JOURNAL OF CATALYSIS 25, 305–313 (1972)

Evidence for the Redox Nature of Zeolite Catalysts

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Received April 26, 1971; revised November 7, 1971

Hydrogen Y-zeolite (HY), under suitable activation conditions, possesses well-marked surface redox properties similar to those described for alumina and for amorphous silica–aluminas of high alumina content. The reducing activity for tetracyanoethylene of sodium-form Y-zeolite 90% exchanged with ammonium ion is intermediate between that of alumina and a silica–alumina cracking catalyst, whereas its oxidizing activity for perylene is considerably greater than that of either. The electron donor sites on the surface of these zeolites may cover a wide spectrum of energies.

Two different surface sites are responsible for the reducing properties of HY. At activation temperatures of around 250°C the site responsible for the reduction of tetracyanoethylene appears to be a surface hydroxyl ion. At higher activation temperatures of around 660°C dehydroxylation of the zeolite leads to the formation of electronegative and electropositive sites which may be the source of the redox activity. Present evidence suggests that site II (which projects slightly outwards from the unshared hexagonal face into the supercage of the zeolitic structure) is the lattice position associated with the electron transfer process.

INTRODUCTION

The surface of activated aluminas and amorphous silica–aluminas of high alumina content possesses well-marked redox properties capable of converting suitable adsorbed molecules into the corresponding radical cations and anions (*1*, *2*). The surface of amorphous silica–aluminas of lower alumina content (∼10%) possesses mainly oxidizing properties with only weak reducing activity (*2*). Although the oxidizing properties of the crystalline aluminosilicates have also been reported (*3*), and the conditions that produce maximum concentrations of surface radical cations have been studied in some detail (*4*), there are few references in the literature to the reducing properties of zeolite catalysts (*5*).

The main result of the present study is to show that a number of zeolite catalysts, under suitable activation conditions, possess well-developed surface redox properties, similar to those already described for alumina.

EXPERIMENTAL

Linde Na-form Type Y zeolite (wt%, dry basis: Na_2O, 12.9; Al_2O_3, 23.1; SiO_2, 64.0) was modified as required by partial exchange of the sodium ion with ammonium ion using methods similar to those of Lunsford (*6*). The aluminium trihydroxide (97% gibbsite, 3% bayerite), subsequently referred to as gibbsite, has been described previously (*7*). The commercial sample of silica–alumina was supplied by Imperial Chemical Industries Limited (Agricultural Division) and contained ∼13% Al_2O_3. It was washed in hot distilled water and dried at 120°C before being activated.

Activation of all catalyst samples involved pretreatment in flowing oxygen in an electric muffle furnace for 1 hr at temperatures between 100 and 1000°C, followed by cooling at 10^{-2} mm Hg over phosphoric oxide for 30 min. The catalyst was then transferred under an atmosphere of dry nitrogen to a standard gas handling system where it was evacuated to 10^{-5} mm Hg; 20 cm of oxygen was introduced, followed by heating for 30 min at the same temperature as that used in the pretreatment. The sample was subsequently outgassed at this temperature for 16 hr at a pressure of 10^{-5} mm Hg or better. The activated catalyst was transferred under an atmosphere of nitrogen to a dry box and added to 5 mm o.d. borosilicate glass tubes containing 2 ml of adsorbate solution.

Tetracyanoethylene (TCNE), 1,3,5-trinitrobenzene (TNB), and *m*-dinitrobenzene (DNB) were all laboratory chemical grade reagents and were purified by standard procedures. Perylene from Rütgerswerke-Aktiengesellschaft was used as received. Benzene (A.R.) was stored over active silica–alumina and filtered before use.

Electron spin resonance (ESR) studies were carried out with a Decca X1 spectrometer operated at 9270 MHz with a magnetic field modulation of 100 kHz. Radical concentrations were estimated by comparison with standard carbon samples which had previously been calibrated with solutions of 1,1-diphenyl-2-picrylhydrazyl in benzene. The error in the determination of radical concentrations was less than ±10%.

RESULTS

Reducing Behavior of Ammonium-Exchanged Zeolites

The number of radicals produced on bringing TCNE, TNB, or DNB into contact with an activated zeolite sample depended markedly on both the concentration of the adsorbate solution (Fig. 1) and the time of contact of adsorbate with the catalyst surface (Fig. 2). Even when apparent saturation of the surface with radicals had been achieved under these conditions, however, irradiation of the catalyst + solution with light from a low-pressure mercury lamp produced a further marked rise in the adsorbed radical concentration. Thus, with TCNE as adsorbate, irradiation for 1 hr increased the radical concentration

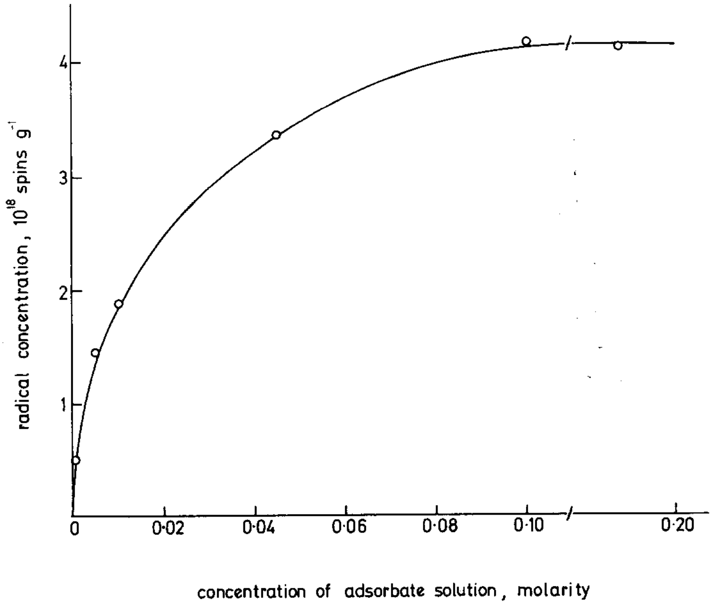

FIG. 1. Radical concentration as a function of TCNE concentration on zeolite 90% exchanged with ammonium ion and activated at 660°C.

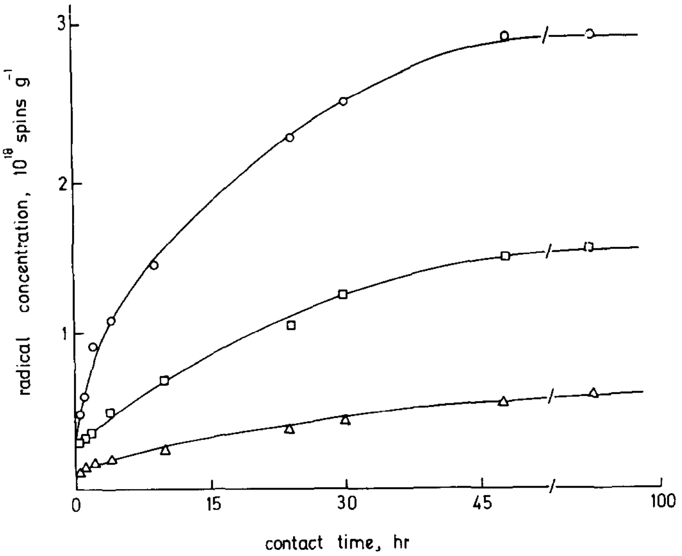

FIG. 2. Radical concentration as a function of time of contact for 0.1 *M* solutions of TCNE (○), TNB (□), and DNB (△) on zeolite 90% exchanged with ammonium ion and activated at 660°C.

by a factor of 1.5; with TNB and DNB the spin concentration was doubled and trebled, respectively. Exposure of the samples to the same source of irradiation for longer periods of time produced no additional increase in radical concentration. For all subsequent measurements of anion–radical concentrations, a 0.1 *M* solution of the adsorbate in benzene was left in contact with the catalyst for 48 hr and the catalyst + solution was then irradiated with ultraviolet light for 1 hr before the ESR spectrum was recorded.

When TCNE was adsorbed at room temperature from solution in benzene on zeolite 90% exchanged with ammonium ion and heated to 150–400°C (subsequently referred to as HY), the surface of the solid acquired a red color and the system gave a nine-line ESR spectrum (Fig. 3a) with a *g* value of 2.0027 and a hyperfine splitting of ~4.9 G; the degree of resolution in the spectrum did not vary with spin concentration. This nine-line spectrum can be assigned to the anion radical of TCNE (*8*). For HY samples dehydrated above 400°C, the ESR spectrum was unresolved (Fig. 3b). The infrared spectrum obtained from the material that was displaced by water from the surface of HY dehydrated above 400°C resembled that given by the polymer of TCNE synthesized by the method of Storbeck and Starke (*9*). A previous investigation (*8*) has shown that this poly-TCNE is paramagnetic and gives rise to an unresolved ESR signal. The effect of variation in the temperature of activation of the catalyst upon the anion–radical concentration is shown in Fig. 4. The maximum number of radicals formed on HY activated at 250°C was $\sim 3 \times 10^{17}$ g^{-1}, corresponding to $\sim 4.5 \times 10^{14}$ active sites m^{-2} of catalyst surface; with samples dehydrated at 660°C saturation occurred when the spin concentration had reached $\sim 4.2 \times 10^{18}$ g^{-1}, i.e., $\sim 7.6 \times 10^{15}$ m^{-2}.

The adsorption of TNB at room temperature from solution in benzene on HY heated at temperatures above 200°C resulted in a three-line spectrum (Fig. 3c) with a hyperfine splitting dependent on the temperature of activation of the catalyst sample: 400°C, separation between outer peaks 64.0 G; 670°C, 68.8 G; 800°C, 67.9 G. Figure 4 shows the corresponding variation of radical concentration with activation temperature of the catalyst. With TNB as adsorbate maximum reducing power was

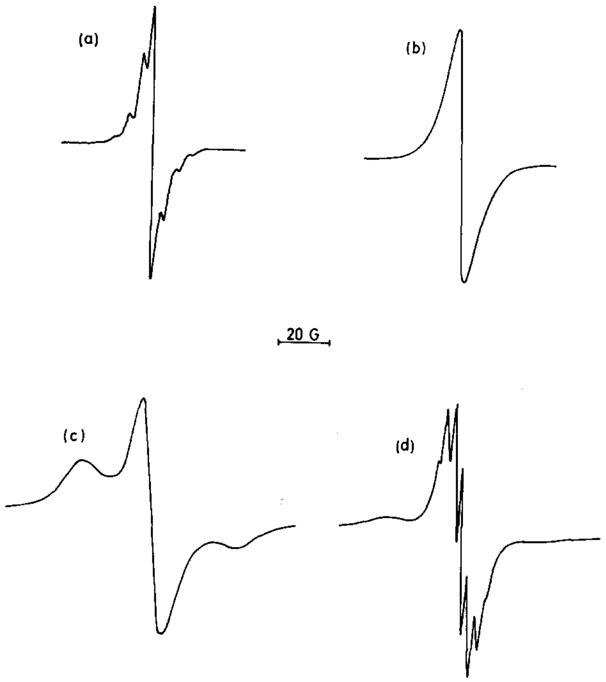

FIG. 3. ESR spectra (first derivative): (a) TCNE on HY activated at 250°C; (b) TCNE on HY activated at 660°C; (c) TNB on HY activated at 660°C; (d) TNB + perylene on HY activated at 660°C.

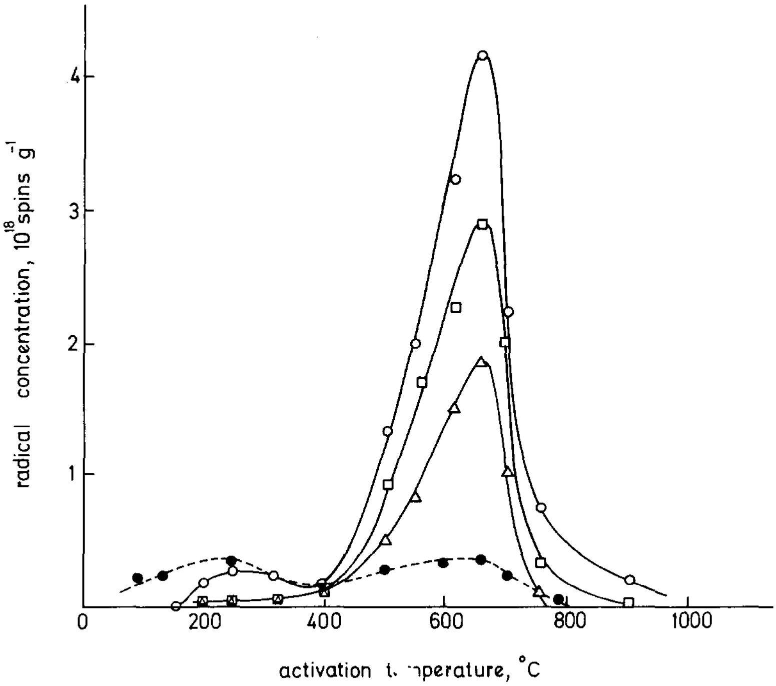

FIG. 4. Reducing activity of HY as a function of activation temperature: TCNE (○); TNB (□); DNB (△). Reducing activity of NaY as a function of activation temperature with TCNE as adsorbate (●).

obtained when the HY was heated at 660°C, the radical concentration being ~2.8×10^{18} g^{-1}, corresponding to ~5.0×10^{15} m^{-2} of catalyst surface.

The substitution of DNB for TNB gave broadly similar results (see Fig. 4), though the optimum radical concentration was lower (~1.8×10^{18} g^{-1}, i.e., ~3.2×10^{15} m^{-2}, for HY dehydrated at 660°C).

Reducing Behavior of Unexchanged Zeolites

Reduction of TCNE occurs on the surface of partially dehydrated Na-form Type Y zeolite (NaY) producing a bright red surface coloration and an unresolved spectrum at all dehydration temperatures. The variation of radical concentration with activation temperature of the catalyst is shown in Fig. 4. Although the curve exhibits two maxima, the optimum spin concentration at the higher activation temperature (~3.1×10^{17} g^{-1} at 600°C, corresponding to ~4.3×10^{14} active sites m^{-2} of surface) is comparable with that observed at lower dehydration temperatures (~3.5×10^{17} g^{-1} at 250°C, i.e., ~4.9×10^{14} m^{-2}).

Reducing Activity as a Function of the Degree of Sodium Exchange

The variation in reducing activity with the ammonium/hydrogen content of the zeolite is shown in Fig. 5. At an activation temperature of 250°C and using TCNE as adsorbate, there was no change in the observed spin concentration as the sodium ions in NaY were replaced by NH_4^+/H^+ ions to the extent of 90%. A change did occur, however, in the shape of the spectrum. For TCNE adsorbed on NaY the ESR spectrum was unresolved, whereas on zeolite samples with 28% or more of the sodium ions exchanged a nine-line signal was obtained. For samples activated at 660°C little change in reducing activity was evident until about 35% of the sodium ions had been replaced, after which an abrupt rise in activity took place (Fig. 5). As the radical concentration increased, the surface coloration changed from bright red to deep red; the observed ESR spectrum was always a singlet. A similar nonlinear change in reducing activity with increasing ammonium/hydrogen content was ob-

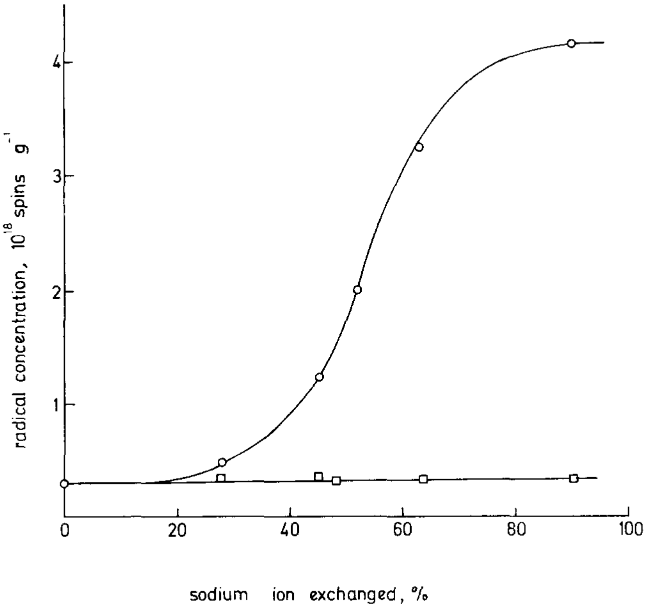

FIG. 5. Reducing activity of HY for TCNE as a function of the percentage of sodium ion exchanged for NH_4^+/H^+: activation temperature, 250°C (□); 660°C (○).

tained when TNB or DNB was substituted for TCNE and the catalyst samples were activated at 660°C.

Reducing Behavior of Amorphous Silica–Alumina Catalysts

With the present TCNE solution, which is fiftyfold stronger than that used in a previous investigation (*8*), two maxima were recorded in the radical concentration against activation temperature plot for a silica–alumina catalyst containing ~13% Al_2O_3 (Fig. 6). At a dehydration temperature of 250°C the spin concentration was ~6.5×10^{17} g^{-1}; for samples activated at 660°C the corresponding figure was ~9.8×10^{17} g^{-1}. The color of the catalyst–radical system was red, and the ESR spectrum was unresolved. For comparison the effect of variation in the temperature of activation upon the radical-forming activity of gibbsite with TCNE as adsorbate is also shown in Fig. 6.

Oxidizing Behavior of Ammonium-Exchanged Zeolites

The oxidizing behavior of HY was investigated using perylene as adsorbate. A saturated solution of perylene in benzene at room temperature (~6.5×10^{-3} *M*) was used and the spin concentrations were determined after 5 days contact with the surface. Samples reached a constant cation–radical concentration under these conditions, and this value was not altered on irradiation with light from the low-pressure mercury lamp. In the presence of oxygen, perylene adsorbed on the surface of HY at room temperature gave a mauve color and an ESR spectrum characteristic of the adsorbed perylenium cation (*7*). The spectrum was fairly well resolved and changed little with time, thus resembling more closely that of perylene adsorbed on amorphous silica–aluminas than that of perylene on an alumina surface. The oxidizing activity of HY as a function of activation temperature is shown in Fig. 7. At the optimum activation temperature of 660°C the perylene radical concentration was ~1.7×10^{19} g^{-1}, i.e., ~3.1×10^{16} spins m^{-2}. With anthracene as adsorbate the radical concentrations were lower than the corresponding values for perylene by a factor of about four. At temperatures above 700°C the crystalline structure of

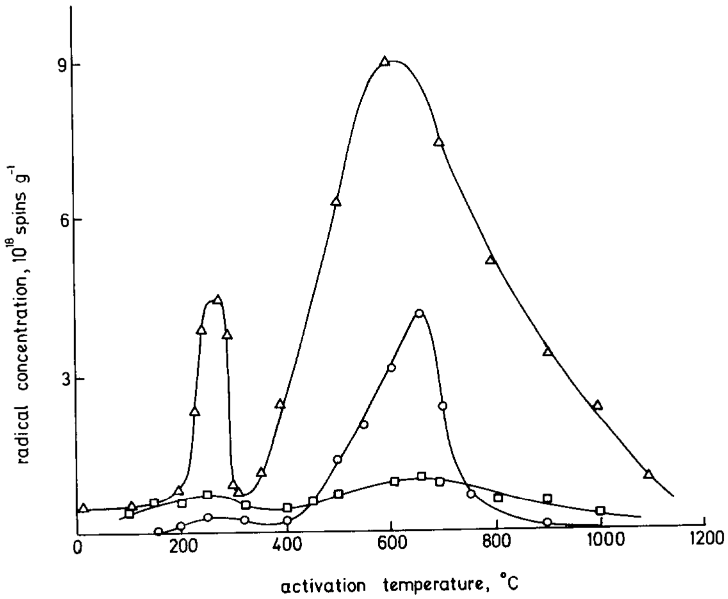

FIG. 6. Reducing activity as a function of activation temperature with TCNE as adsorbate: HY (○); silica-alumina containing ~13% Al_2O_3 (□); alumina (△).

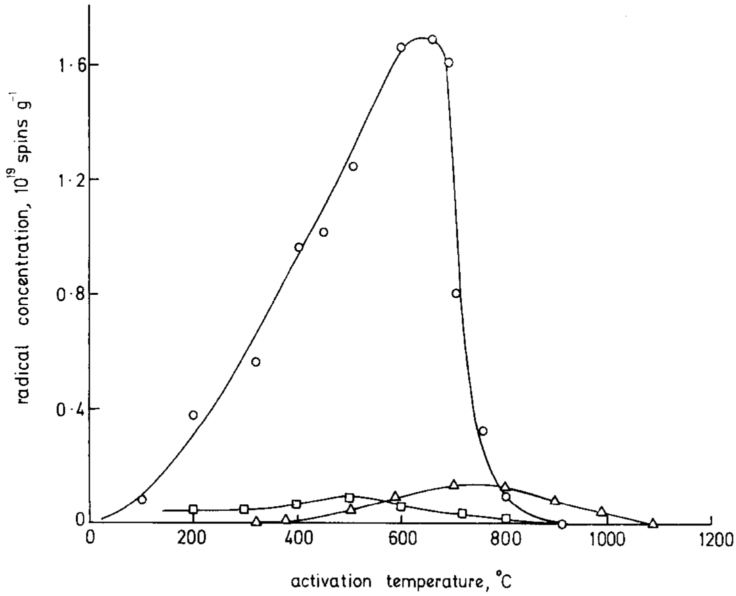

FIG. 7. Oxidizing activity as a function of activation temperature with perylene as adsorbate: HY (○); silica-alumina containing ~13% Al_2O_3 (□); alumina (△).

the zeolite was rapidly destroyed, as shown by X-ray examination, and the electron-transfer power also fell rapidly to zero. Included in Fig. 7 are corresponding data for the perylene + gibbsite system and for perylene adsorbed on silica-alumina containing ~13% Al_2O_3.

Superimposed Spectra

Under certain conditions superimposed ESR spectra of the TNB anion radical and the perylene cation radical have been obtained from the same alumina sample (*1*) and from the same amorphous silica-alumina sample (*2*). Similar spectra have now been obtained on HY (Fig. 3d).

DISCUSSION

Since it has already been shown that hydrogen Y-zeolites possess oxidizing properties and are capable of converting suitable donor molecules into the corresponding cation radicals (*3*), an important result of the present investigation is the demonstration that, like alumina, the zeolites possess well-marked redox properties, when activated under suitable conditions. Two features of the reducing reactions are significant. Firstly, the concentration of anion radicals produced at the surface is a function of the adsorbate concentration (Fig. 1), which implies that an adsorption equilibrium is set up between the adsorbate molecules in solution and the corresponding radical at the surface. Secondly, the radical concentration increases slowly over a considerable period of time (Fig. 2). This observation is important because it means that radical formation occurs not only on the exterior surface, but also in the internal channels and cavities of the zeolite. The increase in radical concentration produced by irradiation may occur as a result of the enhancement of the electron-donating power of marginally weak sites. The number of such sites might be expected to increase with a decrease in the electron affinity of the adsorbed molecule. In accordance with this view the enhancement produced by irradiation is much less with TCNE, a powerful electron acceptor than with the relatively weaker electron acceptors TNB and DNB. Thus, the zeolite surface may contain electron donor sites with a wide spectrum of energies.

The comparison of the redox activity of HY with that of gibbsite and with that of amorphous silica–alumina (~13% Al_2O_3) is of considerable interest (Figs. 6 and 7). In Table 1 these activities have been normalized to unit surface area. Thus, as measured with these adsorbates, the reducing activity of HY is intermediate between that of gibbsite and a silica–alumina cracking catalyst but its oxidizing activity is considerably greater than that of either catalyst. The fact that the radical concentrations obtained with anthracene adsorbed on HY are much lower than the corresponding values for perylene indicates that in this molecular size range ionization potentials rather than differences in molecular dimensions are of prime importance.

Nature of the Electron-donor Sites

Clearly two different surface sites are involved in the reduction of TCNE (Fig. 4), one responsible for the shallow maximum in activity at activation temperatures around 250°C and another responsible for the main reducing activity produced by activation around 660°C. Significantly, the reducing activity at the lower temperature is independent of the extent of sodium exchange and the site responsible for this activity is too weak to convert either TNB or DNB into the anion radical. As in aluminas activated at low temperatures (*8*), the reducing agent here may be an hydroxyl ion. At higher activation temperatures of around 660°C, dehydroxylation of the hydrogen zeolite leads to the formation of possible electron donor and acceptor sites according to the following scheme:

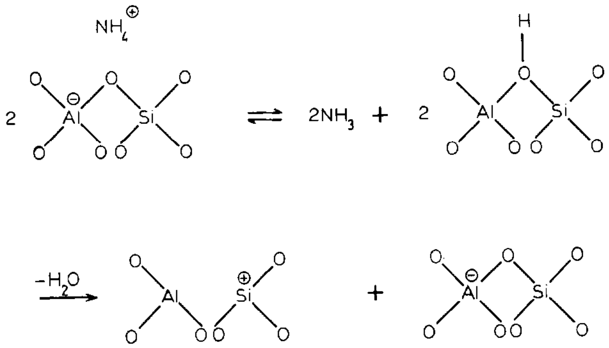

TABLE 1

OPTIMUM SPIN CONCENTRATIONS WITH TCNE AND PERYLENE AS ADSORBATES

Catalyst	Spin concn. with TCNE as adsorbate, 10^{15} spins m^{-2}	Spin concn. with perylene as adsorbate, 10^{15} spins m^{-2}
HY	8	31
Alumina	45	7
Silica–alumina (~13% Al_2O_3)	3	2

Such electropositive and electronegative sites produced by dehydroxylation may be the source of redox activity in zeolites. If this is the case, however, it must be assumed that only a small proportion of the possible sites [~1 × 10^{21} g^{-1} (*4*)] have sufficient energy to act as reducing agents for the electron acceptors TCNE, TNB and DNB or as oxidizing agents for perylene, or alternatively that only a small proportion of the possible sites are accessible. Figure 5 provides evidence that some at least of the sites are inaccessible to TCNE, since up to 35% replacement of Na^+ by NH_4^+ produces little change in reducing activity.

X-Ray structural studies (*10*) of dehydrated NaY have shown that the sodium ions occupy three positions in the crystal lattice: site I at the center of an hexagonal prism, site I′ displaced from a shared hexagonal face into the sodalite cage, and site II slightly displaced from an unshared hexagonal face into the supercage. About 58 sodium ions per unit cell are required to balance the aluminum atoms. The distribution of these cations, as estimated from X-ray analyses, has been given (*11*) as: site I, 7.5 ± 0.5; site I′, 19.5 ± 0.5; site II, 30.0 ± 0.5. In a study of the exchange adsorption of ammonium ions by zeolite Y at room temperature (~20°C), Theng, Vansant, and Uytterhoeven (*12*) found that only 70% of the sodium ions could be replaced and attributed this to the inaccessibility of the cubo-octahedra to the ammonium ion, the exchange reaction being confined to the large cavities. When the exchange is carried out at higher temperatures, however, it seems that the sodalite cages can be penetrated by ammonium ions. In the present experiments, following the Lunsford technique (*6*), 50% exchange of the sodium ion was obtained when the reaction was conducted at room temperature; with repeated exchange at 80°C, 90% of the sodium ions were replaced. These findings are in close agreement with those of Lunsford (*6*). By repeatedly contacting NaY with an aqueous solution of ammonium chloride at refluxing temperature, Bolton and Lanewala (*13*) obtained 95% replacement of the sodium ion. It appears therefore that under suitable experimental conditions the sodium ions occupying the I′ sites can be replaced.

If the I′ sites are accessible to ammonium ions but not to the molecules of the organic adsorbates used, the abrupt rise in reducing activity between the 35% and 80% exchange levels might suggest that site II is the lattice position associated with the electron transfer process (calculated on the basis of the figures quoted: all I′ sites are exchanged after 34% of the sodium ions have been replaced; all site II positions at 87%).

At activation temperatures above 700°C both the reducing and the oxidizing activity of the zeolite fell rapidly (Figs. 4 and 7) as a result of the collapse of the crystalline structure shown by X-ray examination. This decay of the crystal structure and the accompanying reduction in the BET surface area would indicate that the HY used in the present study was the normal hydrogen Y zeolite rather than the "ultrastable" type (*14*).

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