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Studies of the Hydrogen Held by Solids

XXI. The Interaction Between Ethylene and Hydroxyl Groups of a Y-Zeolite at Elevated Temperatures

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The infrared spectra of the OH groups of a hydrogen-Y-zeolite have been recorded in the presence of C_2H_4 at pressures up to 1 atm and in the temperature range 25 to 150°C. From these data, the heat of formation of hydrogen-bonded C_2H_4 was estimated to be about 9 kcal $mole^{-1}$ for interaction with the 3648 cm^{-1} groups. Isotopic exchange between C_2D_4 and the two principal types of OH groups was studied at temperatures between 200 and 350°; both exchanged at about the same rate. Equilibration of C_2D_4 and C_2H_4 proceeded via exchange with the surface OH groups. C_2D_4/OH exchange took place 1.2 times faster than C_2H_4/OD exchange over zeolite samples pretreated in equivalent ways. The kinetics deviated slightly from a first order dependence on the distance from equilibrium. The apparent first order rate constants reached an apparent maximum for pretreatment at 290°C. The apparent activation energy for exchange was 16 kcal $mole^{-1}$ for samples pretreated at 290°C and 19 kcal $mole^{-1}$ for those heated at 475°C in O_2 and rehydrated at 350°C. In both instances, the reaction was first order in C_2D_4 pressure.

INTRODUCTION

Substantial advances in our understanding of acid catalysis have been made during the last decade. Tracer and kinetic studies of the reactions of simple molecules over aluminum silicates have confirmed their carbonium ion character and have defined their reaction coordinates. From the latter, insight into the origin of selectivity has been obtained and the variable nature of the intermediate was revealed. It has been demonstrated (*1*) that a given carbonium ion is not exactly the same species on all surfaces because of changes in the reaction coordinates, e.g., in the relative heights of the barriers between the carbonium ion and the several products. In this way, it has been possible to draw the diverse ideas found in the literature (*1–9*) into a unified picture. These concepts have suggested that, in many cases, the rate-determining step should be the formation of the metastable carbonium ion from the adsorbed substrate so that the true activation energy for the reaction is that for ion formation (*9*).

It has become abundantly clear that, whatever the nature of the catalytic sites, the reactions are proton catalyzed. The discovery (*10*) that triphenylmethane is converted by silica–alumina into the triphenylcarbonium ion by a reaction involving Bronsted, rather than Lewis, sites has cast doubt on the existence of intrinsic Lewis centers capable of removing H^- from hydrocarbon molecules. However, it now seems probable that polymeric "residue" carbonium ions serve as the catalytic sites on silica–alumina catalysts (*2, 3, 7, 11–13*). Ozaki and Kimura (*7*) suggested that the

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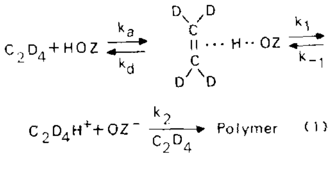
initial monomer adsorbed on a Lewis site; Hightower and Hall (*2*) proposed that proton donating polymeric residues formed on either Lewis or Bronsted sites; Clark and Finch (*12*) established that the average residue contained about four monomeric units, and Hirschler (*13*) has extracted and characterized this material as a mixture of polymeric monoolefins. The simplest interpretation is, therefore, that polymeric olefins form and remain strongly adsorbed on Bronsted sites. Periodically they become carbonium ions and, since they block the sites, act as transfer agents for protons between catalyst and substrate. According to Hirschler (*13*), the same sort of polymeric residue forms within the HY-zeolite as on silica–alumina catalysts. Studies with HY have added much to our understanding of solid acids because its Bronsted sites can be seen spectroscopically (*14*).

The formation of polymeric residue on the HY-zeolite was studied spectroscopically by Liengme and Hall (*15*). Infrared measurements showed that, at room temperature, C_2H_4 molecules were adsorbed by hydogen-bonding to the acidic hydroxyl groups which, when unperturbed, gave rise to the sharp absorption band at 3648 cm^{-1}. Comparison with adsorption isotherms determined with a BET system, confirmed that this was the principal interaction. Both kinds of measurements showed that the adsorption was rapidly reversible on fully hydroxylated samples below 100°. Although the interaction was strong ($\Delta\nu = 350\ cm^{-1}$), no isotopic exchange occurred between C_2D_4 and the zeolite OH groups. At higher temperatures ($\sim$200°C), however, exchange was observed and this was accompanied by polymerization and subsequent cracking. Pyridine reacted quantitatively with these same OH groups at room temperature to form pyridinium ion.

A similar, but significantly different, behavior was found when C_3H_6 was substituted for C_2H_4. The hydrogen-bond was stronger ($\Delta\nu = 450\ cm^{-1}$); much lower pressures were required to cover the same number of sites. Isotopic exchange and polymerization took place slowly at room temperature; after several days, no propylene was left in the gas phase; and the spectrum characteristic of hydrogen-bonded simple olefin was replaced by that for the zeolite immersed in polymer. Presumably, had we been able to work at lower temperatures and pressures, the behavior of C_3H_6 would have resembled that of C_2H_4. Eberly (*16*) has reported qualitatively similar behavior for other aliphatic olefins.

Liengme and Hall (*15*) explained the adsorption by hydrogen-bonding in terms of charge-transfer theory with an excited state differing from a classical carbonium ion only in possessing some "no-bond" character and, hence, different bond angles and lengths. Although the Franck-Condon principle would require a very high energy for the direct optical transition to the unrearranged excited state, *thermal* activation to the classical carbonium ion could occur much more readily through readjustment of nuclear coordinates to the configuration of minimum energy. The greater reactivity of C_3H_6 was attributed both to its stronger interaction with hydroxyl groups, and to the lower energy of the *sec*-propyl carbonium ion compared with the primary $C_2H_5^+$ ion which would be formed from C_2H_4. It was shown, however, that the same zeolite chemisorbed ethylene *irreversibly* at room temperature when it was 92% dehydroxylated and that i-C_4H_{10} and i-C_4H_8 appeared in the gas phase on heating to 120°. Turkevich *et al.* (*17*) reported that C_2H_4 polymerized at 100°C over a decationated X-zeolite and that the activity per site increased with the site density. Thus, polymeric material will form from either C_3H_6 or C_2H_4 and deposit in the zeolite; the extent will depend on the olefin, the temperature, and the condition of the surface. It is too soon to assess the extent to which the residue may moderate the catalytic behavior.

The clean HY may be studied in reversible interactions with various bases as can the catalyst covered with polymeric residue. The former relates to most spectroscopic examinations and the latter to most catalytic measurements. The present work may be regarded as a probing mission designed to seek ways to bridge the two systems. The problem may be formulated as follows:



(1)

where k_a and k_d are rate constants for adsorption and desorption of the hydrogen-bonded olefin, respectively; k_1 and k_{-1} are the forward and reverse rate constants for formation of the carbonium ion from the hydrogen-bonded species, and k_2 is the rate constant for polymerization. The various steps in this scheme are amenable to study by *in situ* infrared methods. If the activation energy for the overall reaction is associated with carbonium ion formation, i.e., with k_1, the adsorption–desorption step will be isolated at sufficiently low temperatures. It is here also, that large fractional coverages occur so that the heat of adsorption can be conveniently measured by the method of Hertl and Hair (*18*). Heats of adsorption of ethylene on metal ion exchanged zeolites have been chromatographically (*20*), but measurements are lacking for decationated zeolites with their much higher concentrations of surface hydroxyl groups.

At higher temperatures, exchange should occur between the olefinic deuterium and the acidic OH groups of the zeolite. On the basis of the model, the activation energy for this process should be that for carbonium ion formation. This parameter can be measured provided the exchange kinetics are uncomplicated and that leakage into product residues, k_2, is not too large. We have studied the exchange kinetics between C_2D_4 (or C_2H_4) and zeolite OH (OD) groups in the temperature range 200 to 300°C. Carter *et al.* (*21*) applied room temperature infrared measurements to follow the course of exchange between D_2 and the OH groups of η-Al_2O_3 at 250°C, but the measurements reported herein are believed to represent the first case in which this technique has been used at elevated temperatures.

Experimental Methods

Equipment. All spectra were recorded using a Beckman IR-12 spectrometer operating in the linear absorbance mode with low amplifier gain and wider than normal slit widths. With these conditions, it was possible to achieve a reproducibility of ±0.5% in apparent optical density. The spectral slit width was about 4 cm^{-1}, or $\frac{1}{7}$ to $\frac{1}{5}$ of the half-widths of the higher frequency of the two OH and OD bands. It was estimated from the data of Ramsay (*22*) that the measured optical densities were lower than the true ones by about 4% (due to instrumental broadening); but since only relative values were required, corrections were unnecessary. Spectra of samples at temperatures above 150°C were recorded with the spectrometer chopper between the sample and detector disconnected in order to avoid errors due to emission by the sample (*23*).

The silica infrared cell used in the measurement of the heat of adsorption of ethylene on the zeolite was described elsewhere (*23*). The cell used in the exchange work consisted of a 250 ml bulb to which was attached a 15 cm extension of 1.5 cm tubing terminating in a silica infrared cell of 0.2 cm path length. It was protected by traps cooled to —196 and —80°C, respectively, from the pumping and pressure measuring sections of the system. The entire cell was heated to nearly 200°C during pretreatment to eliminate adsorbed water. The infrared section of the cell was fitted inside an aluminum block within a furnace; the catalyst temperature could thus be maintained constant to ±0.1°C over the several day period of each experiment.

Materials. The NH_4^+-zeolites were prepared from the parent NaY form (obtained from the Linde Co.; Lot No. 1280-133). The calcium content (0.4% in the parent zeolite) had been reduced to 0.02 to 0.03% (*4*). For the present work, two samples were used. For the adsorption studies, 66% of the Na^+ ions were replaced by NH_4^+, whereas only 57% were replaced in the preparations used for studies of the isotopic exchange.

The C_2H_4 used was Lif-o-gen Research Grade; it contained no detectable impurities. The C_2D_4, as obtained from several commercial sources, was found to contain a combined total of up to 0.5% propylene and butenes, which were removed by preparative gas chromatography to a level of $<0.01\%$. Mass spectral analysis showed that the overall amount of H present (as C_2HD_3) was 1.1%.

Techniques. Spectroscopic platelets approximately $28 \times 12 \times 0.2$ mm (weighing 2.5 to 6.0 mg cm^{-2}) were prepared by compressing the powdered zeolites at 10,000 psi for 2 min. These were pretreated *in situ* by two methods in the infrared cells. Method I consisted of evacuating the sample for a few minutes at room temperature and then slowly raising the temperature (1.5°C min^{-1} to 200°C, 4°C min^{-1} above 200°C) to a level adequate to remove all evidence of NH bands in the spectrum (above 250°C). The final temperature employed was 290°C except in some initial experiments designed to determine the effect of pretreatment temperature on exchange rate or where Method II was employed. Method II was similar to that described by Liengme and Hall (*15*). It comprised the steps outlined above for Method I followed by calcination in O_2 for 0.5 hr at 475°C (to remove any carbonaceous material), evacuation at 475°C, exposure to 10 Torr H_2O vapor at 350°C (to restore, in part, the small number of hydroxyl groups lost at 475°C) and evacuation at 350°C for 1 hr to a pressure of about 10^{-6} Torr.

The pretreated samples were cooled to the selected experimental temperatures and the spectra were recorded from 2400 to 4000 cm^{-1}. For adsorption experiments, spectra were determined at several temperatures at fixed C_2H_4 pressure; this was repeated for several C_2H_4 pressures. For the exchange experiments, a measured quantity of C_2D_4 was condensed into a sidearm on the cell. The reaction was commenced by vaporizing the C_2D_4 and simultaneously setting the instrument to scan repeatedly over the OD region of the spectrum. The repetition rate could be varied from once every 20 to once every 180 min by the aid of a timer. When the rate of exchange had fallen to very low values, the gas phase was removed for mass spectral and gas chromatographic analysis and the spectrum of the remaining OH groups was recorded. Values of Y_∞ were calculated from the mass spectral data, *vide infra*.

Theory. If there are N_s hydroxyl groups exchanging with N_g ethylene molecules and if the atom fraction H (of the OH + OD) is Y, then the number of OH groups remaining at any time is YN_s. If the exchange is simple (all exchanging H or D equivalent in each phase), then the exchange law (*24*) is

$$N_s(dY/dt) = R[(4N_g + N_s)/4N_g](Y_\infty - Y). \tag{2}$$

On integration, the familiar first order dependence on the distance from equilibrium is obtained with the characteristic slope parameter,

$$k(\text{min}^{-1}) = R(4N_g + N_s)/4N_gN_s. \tag{3}$$

In this development, R is the rate (atoms min^{-1}) at which H flows between equivalent sites in C_2H_4 and in the OH groups. This process occurs continuously, but requires tracers to measure. R is the rate of a process at equilibrium; it varies with temperature and pressure in ways which reflect the mechanisms of the steps involved. In the present work, the experiments were arranged so that $N_g \gg N_s$ (from 4 to 14 times). With this constraint

$$k(\text{min}^{-1}) \approx R/N_s, \tag{4}$$

since N_s is constant, k contains the same information as R and effects of variation in gas pressure (N_g) will appear only as changes in R.

There are at least two different OH species in the hydrogen zeolite. One of these vibrates into the supercage where it can interact directly with C_2H_4; the other may not (*15*). If exchange takes place between olefinic hydrogen and the first kind, and if the second then exchanges with the first, the kinetic plots will deviate from linearity *unless* the second process is much faster than the first. The general exchange law is known (*25*); it is a sum of exponential functions. Hence, if the second step is slower than the first, curvature toward decreasing slope with increasing time will appear on the usual first order plot.

RESULTS

The heat of adsorption. Representative spectra showing the interaction of C_2H_4 with the hydroxyl groups of a pretreated (by Method II) zeolite platelet are given in Fig. 1. The room temperature data were equivalent to those reported earlier (*15*), the principal characteristics being a relatively large decrease in the intensity of the 3648 cm^{-1} OH band, and the appearance of a band at about 3300 cm^{-1} due to the ethylene-hydroxyl group complex. Except for relative intensities, these features were unchanged over the temperature range 25 to 125°. The 3550 cm^{-1} band may have decreased in intensity also, but this was at least 3 to 4 times smaller than the corresponding decrease of the 3648 cm^{-1} band. The peak frequency of the 3300 cm^{-1} band possibly shifted slightly to higher frequency at the higher temperatures, but weak bands due to the stretching vibrations of adsorbed ethylene (not shown) were unaffected. The changes brought about on admitting C_2H_4 to the cell were fully reversed on evacuation and, at the maximum temperature at which adsorption by hydrogen-bonding could be detected (~150°), no polymerization occurred (as was revealed by the absence of any residual CH bands in the spectrum following evacuation).

From a series of spectra, the variation in the intensity of the 3648 cm^{-1} OH band with ethylene pressure was obtained at a number of constant temperatures. These data were expressed in the form of isotherms by defining

$$X = \frac{I_0 - I_p}{I_0},$$

where I_0 was the optical density under vacuum and I_p the corresponding value with P Torr of C_2H_4 in the cell. Thus, X is the fraction of OH groups interacting with P Torr of C_2H_4. For our purposes it was convenient to plot log X versus log P. Smooth curves were formed which decreased monotonically in slope with increasing pressure and had evenly spaced points; the variation of log P with temperature for constant values of X was

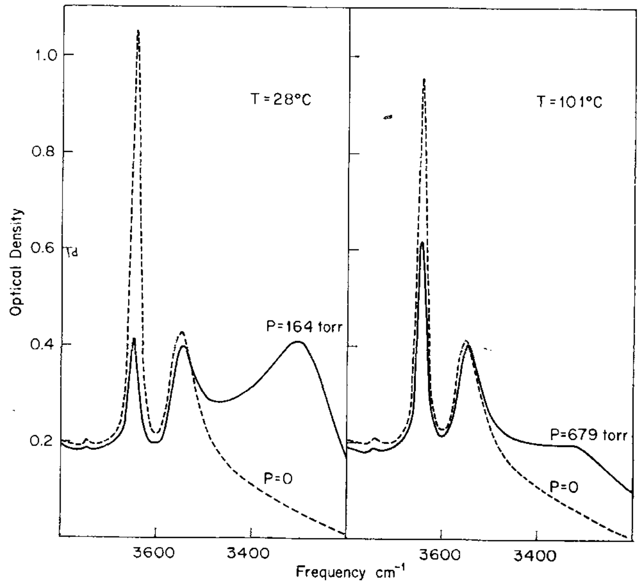


FIG. 1. Infrared spectra of hydroxyl groups of Y-zeolite in presence of ethylene gas.

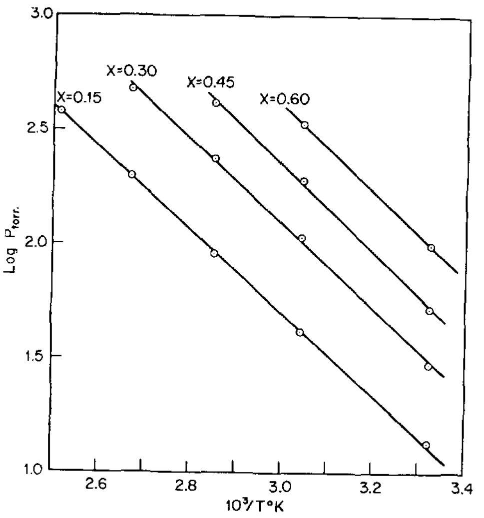


FIG. 2. Clausius-Clapeyron plots for adsorbed ethylene at various X-values.

obtained by interpolation. These data are plotted in Fig. 2. All the data fell on good straight lines from which the heat of adsorption was estimated to be 8.4 ± 0.3 kcal mole^{-1}, independent of X (i.e., of coverage).

The exchange reaction. Initial attempts to measure rates of exchange between C_2D_4 (or C_2H_4) and OH (OD) groups of several zeolite samples produced discordant results. The first order plots were not linear and under some circumstances increased in slope as the reaction proceeded. This unusual behavior indicated an induction period, thus implying that additional exchange pathways were being developed and superimposed on the chemistry of Eq. (1). Moreover, the groups giving rise to the 3648 and 3550 cm^{-1} absorptions were not converted to their OD analogs (absorbing at 2685 and 2630 cm^{-1}) at the same rate; the form of the kinetics differed for the appearance of OD groups compared with the disappearance of OH groups and furthermore was not the same as observed in C_2H_4/OD exchange experiments. These peculiar findings were due to the incorporation of some of the OH (or OD) groups producing the high frequency absorption band into irreversibly chemisorbed residue. The existence of a polymer was demonstrated by the development of CH (CD) stretching bands which remained after removal of the gas phase at the conclusion of each experiment and by the fact that the platelet was then yellow-grey in color. The evolution of considerable CO_2 on subsequent calcination in O_2 provided further confirmation.

Residue formation was traced to a variety of causes. Polymerization appeared to be favored by dehydroxylation of the zeolite or the presence of divalent cationic impurities. Traces of higher olefins in the C_2H_4 enhanced the rate of this process. Sample contamination also appeared to stem from impurities from the vacuum line in the form of hydrocarbon lubricants and adsorbed water. The latter provided an additional source of hydrogen to exchange with the zeolite. Consistent data were obtained only after the procedures and materials described in the experimental section were adopted. With these preparations, exchange was immeasurably slow below 120°C; it occurred at a conveniently measurable rate between 200 and 350°C.

The results of the exchange experiments were plotted as the log $(Y - Y_\infty)$ vs time. Allowance was made for the fact that the apparent extinction coefficients of the OH and OD groups were not the same (the former were larger by about 10%). Typical results are given in Fig. 3. These data show the effect of pretreatment temperature (according to Method I) on exchange

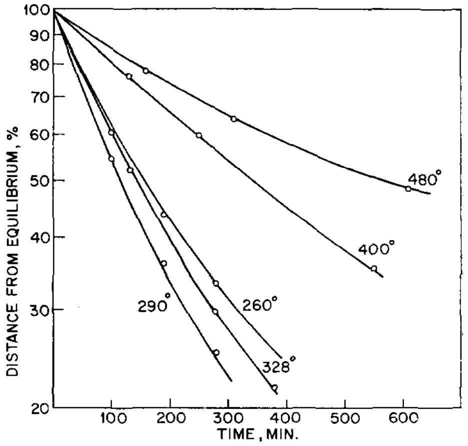


FIG. 3. Effect of pretreatment temperature on exchange rate at 262°C using 26 Torr C_2D_4.

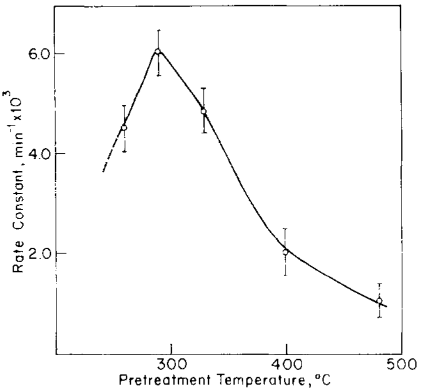


FIG. 4. Effect of pretreatment temperature on the apparent rate constant at 262°C using 26 Torr C_2D_4.

rates at 262°C. In each experiment a new platelet was reacted with 26 Torr of C_2D_4. The lines represent the data for the 3648 cm^{-1} band; the open circles are results for the 3550 cm^{-1} band. The concordance of the points and lines demonstrate that both types of OH groups exchanged at about the same rate. The first order rate constants of the reactions, as estimated from the initial slopes of the curves, are plotted against pretreatment temperature in Fig. 4.

Arrhenius plots for the reaction between C_2D_4 and OH groups of zeolites are given in Fig. 5 and the effect of ethylene pressure is shown in Fig. 6. In both Figs. 5 and 6, the open circles represent experiments in which new platelets were pretreated by either of the two methods while closed circles indicate experiments in which a previously used platelet was pretreated a second time by Method II and reused. The data for experiments using new and reused samples (Method II) fell on the same straight line from which an activation energy of 19 kcal $mole^{-1}$ was calculated; a value of 16 kcal $mole^{-1}$ was obtained for the samples pretreated by Method I. For both pretreatment methods, k, and therefore R, increased linearly with C_2D_4 pressure. The *adsorption* was too small to observe spectroscopically at the experimental temperature. Consequently, it may reasonably be supposed that the adsorption required for the exchange lies in the Henry's law region, i.e., that R is linear in X.

One sample was pretreated at 290°C by Method I, cooled to 251°C and exposed to a mixture of C_2H_4 (26 Torr), C_2HD_3 (0.6 Torr), and C_2D_4 (27.4 Torr). The course of the $OH \dashrightarrow OD$ exchange and the increase in C_2HD_3 concentration with time are plotted in Fig. 7. The rate constant for the former was about 7×10^{-3} min^{-1} and, since the initial number of OH groups in the platelet was about 2.8×10^{19}, the rate of transfer R was approximately 20×10^{16} atoms min^{-1}. Isotopic scrambling

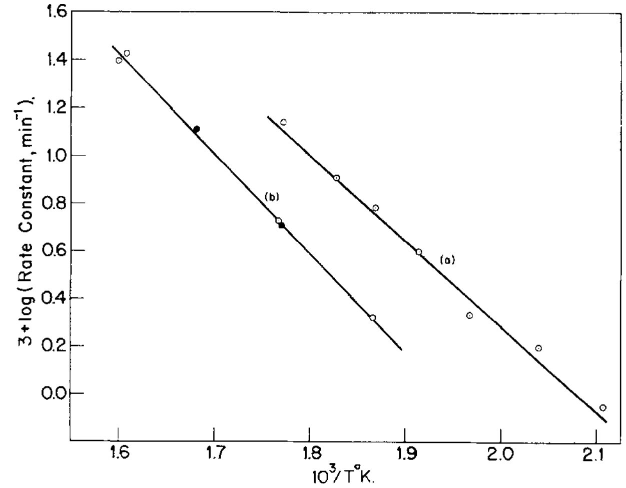


FIG. 5. Effect of temperature on the amount rate constant for OH/C_2D_4 exchange with C_2D_4 pressure of 26 Torr: (a) samples pretreated by Method I; (b) samples pretreated by Method II.

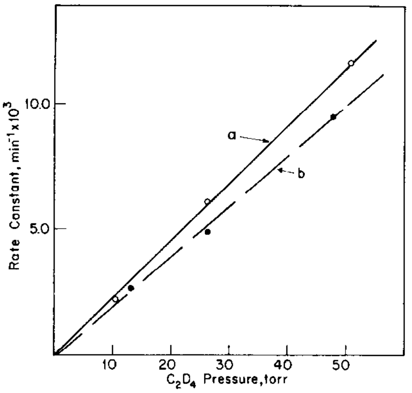


FIG. 6. Effect of C_2D_4 pressure on the apparent rate constant for C_2D_4/OH exchange: (a) at 261°C for samples pretreated by Method I; (b), at 292°C for samples pretreated by Method II.

between C_2H_4 and C_2D_4 occurred at about the same rate. The C_2HD_3 concentration increased with time between 0.01 and 0.03% min^{-1}. Since the total number of D atoms in the ethylene molecules admitted was 10.2×10^{20}, the initial rate of transfer of hydrogen into the C_2D_4 was between 10 and 30×10^{16} atoms min^{-1}. Thus, C_2H_4/C_2D_4 scrambling evidently occurred via catalyst OH and OD groups.

Isotope effects were minimal. A new platelet of the Y-zeolite was evacuated at 290°C, exposed to a large excess of D_2O vapor (10 Torr) for a total of 30 min. After evacuation for 1 hr at 290°C, it was cooled to 261°C; and the exchange reaction with 26 Torr of C_2H_4 followed for 12 hr. Another platelet was treated in an identical way, except that it was equilibrated with H_2O and exchanged with C_2D_4. The results are shown in Fig. 8. Both curves showed the usual slight deviation to lower rate at high conversions. The system OH/C_2D_4 reacted somewhat faster than OD/C_2H_4, but this kinetic isotope effect was only about 1.2.

Proton resonance spectra from the HY, taken at several temperatures, is shown in Fig. 9. These experiments will be detailed elsewhere (*26*), but these data demonstrate the mobility of the hydrogen in the solid.

DISCUSSION

An implicit assumption in the present work was that all groups contributing to the OD and OH absorption bands have identical molecular extinction coefficients which were unaffected by adsorption of ethylene onto neighboring sites. The quan-

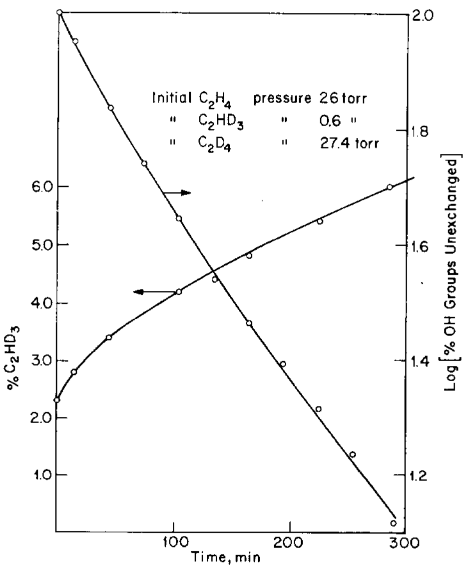


FIG. 7. Exchange between OH groups and 1:1 C_2H_4/C_2D_4 mixture at 251°C.

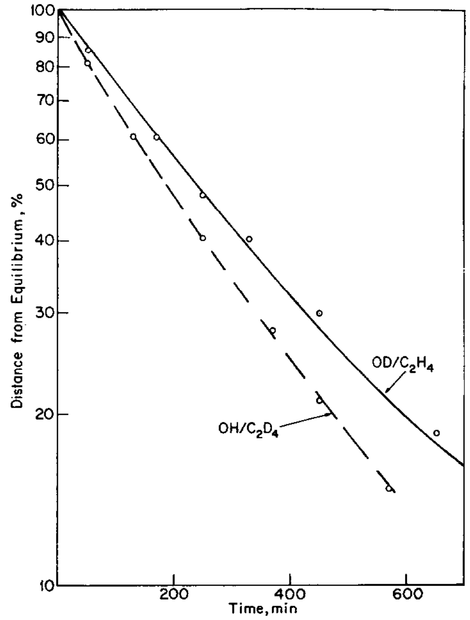
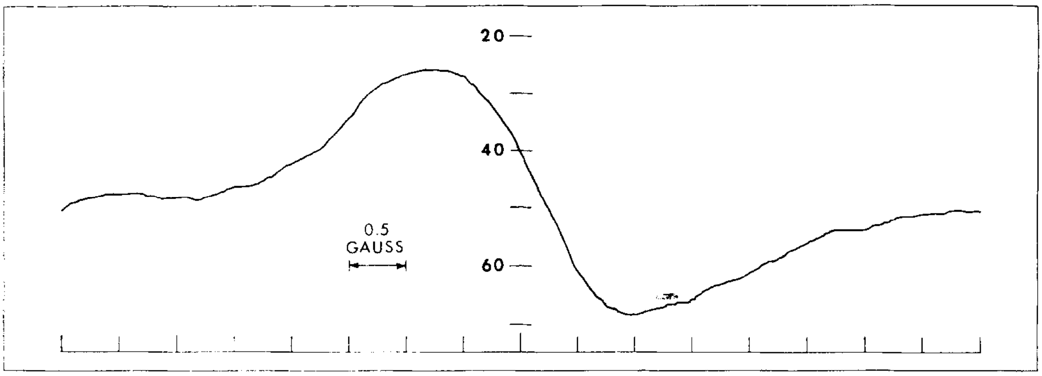
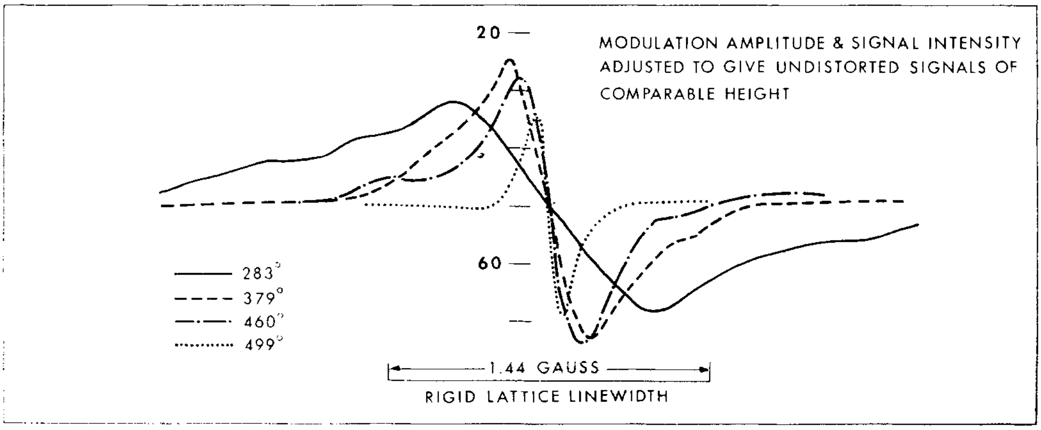


FIG. 8. Dependence of the rate on direction of exchange at 261°C with ethylene pressure of 26 Torr.



(a) ROOM TEMPERATURE SPECTRA



(b) SPECTRA AT VARIOUS TEMPERATURES

FIG. 9. Proton resonance of HY-zeolite.

titative spectroscopic measurements of Hughes and White (*27*) have shown this to be true for the adsorption of pyridine on similar Y-zeolites.

As has been pointed out by Hertl and Hair (*18*), an advantage of the spectroscopic method for determining heats of adsorptions is that only the interaction with a single well-defined site is measured. Thus, in the present systems, other methods would contain contributions from adsorption onto residual Na^+ ions and on other parts of the surface, whereas only the interaction with the specific OH groups producing the 3648 cm^{-1} adsorption band was measured spectroscopically. The constancy of the heat of adsorption up to quite high coverages indicates that these OH groups are all very similar in acidity. This may be generally true for well-defined OH groups, since similar observations have been made with a well-degassed silica (*18*).

The Langmuir isotherm describes an adsorption process where gas molecules interact with isolated identical centers; the adsorbate–adsorbent interaction energy is constant and not a function of coverage; the adsorbate–adsorbate interaction is negligible. The present system appears to fit this description. The data plotted in Fig. 10 conform very closely to the Langmuir equation at the three lower temperatures. At the higher temperatures, the intercepts appear low, suggesting that some other requirement for Langmuir adsorption is not being met. Possibly, the total number of adsorption sites is not constant. The NMR measurements (*26*) have shown that

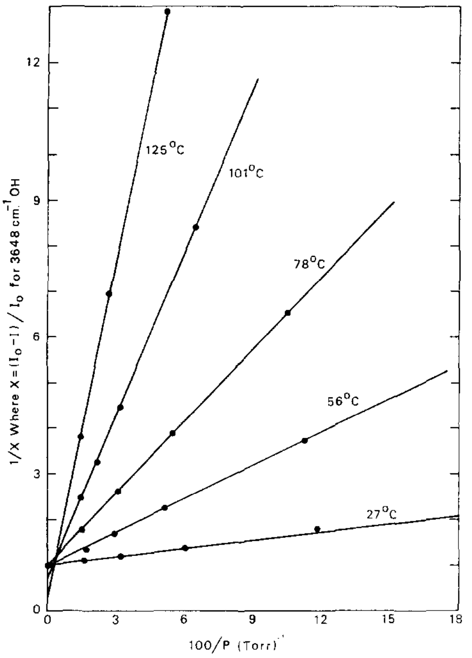


FIG. 10. Langmuir plots for adsorbed C_2H_4.

the H atoms of HY are mobile (time constant 10^{-3} to 10^{-5} sec at the temperatures of interest here). IR results (*28*) suggest a redistribution of protons over the lattice oxygen positions with changes in temperature. In the present work (Fig. 1), the intensity of the 3550 cm^{-1} band was decreased somewhat by the adsorption of C_2H_4, although direct interaction between this gas and the corresponding OH group is not possible. Similarly, both types of OH groups underwent exchange with C_2D_4 at the same rate. Therefore, an increasing fraction of the hydrogen from groups which are not directly accessible to the gas phase may become trapped by the adsorption process on external sites as the coverage increases. The heat of adsorption calculated from the slopes of the plots of Fig. 10 was 9.5 ± 0.6 kcal $mole^{-1}$, in fair agreement with that from the Clausius-Clapeyron method.

The heat of adsorption and frequency shift (350 cm^{-1}) corresponding to the hydrogen-bonding interaction lie within the rather wide limits quoted by Pimentel and McClellen (*29*). Therefore, although the process has the properties of a strong physical adsorption, it involves a very specific interaction, probably of the charge-transfer type (*15*).

Liengme and Hall (*15*) suggested that exchange and polymerization are intimately related by the chemistry of Eq. (1); both involve the formation of the same intermediate carbonium ion. This picture was supported by the fact that the same acidic hydroxyl groups react with NH_3 (*14*) and nitrogen bases (*14–16, 27*) to form the corresponding ions and by the fact that HY is a very effective catalyst for reactions involving carbonium ions. It was further supported by the observations that the exchange and polymerization reactions appeared inseparable and that the stronger the hydrogen bond, the more readily these processes occurred. The present results suggest that the transition state for the exchange reaction is not identical with that required for polymerization. In fact the data could be just as well satisfied if the processes were completely independent. At exchange temperatures, the adsorption was too small to detect spectroscopically. Since the hydrogen in the solid was mobile well within the experimental time scale (*26*), the exchange could occur on a small portion of the sites, or at impurity centers, and the isotopes could mix by diffusion throughout the solid.

The inverse dependence of the exchange rate on pretreatment temperature (Fig. 4) is antiparallel to the catalytic activity for acid catalyzed reactions. The latter increases with activation temperature to a maximum between 500 and 600°C (*30–32*). If exchange were occurring at only a relatively few very strong sites followed by mixing by proton diffusion, the results in Fig. 4 could stem from site deactivation (for exchange) by residue formation. However, no evidence for deposition of this carbonaceous material was found in the CH stretching region of the spectra, but this could not be expected if the fraction of active sites were very small. Hildebrandt and Skala (*33*) have shown that, following evacuation at 400°C, NH_4Y retained a very small fraction of its NH_3, even though the IR spectra showed no NH bands. It was this NH_3 chemisorption which reproduced the activity volcano of Venuto *et al.* (*31*). Although the details are not clearly understood, it would appear that as these very strong sites are made available, sites for carbonium ion catalysis are generated, possibly through residue formation, while sites for exchange are removed or reduced in number by as much as a factor of five.

Pretreatment procedures I and II were devised so that interpretable kinetic results could be obtained. Only in this way could the reaction be studied over a wide range of temperature without substantial polymerization. Such spectroscopic platelets remained white at the conclusion of the experiments, and their spectra showed no evidence of CH bands, although a small amount ($\sim$0.05%) of ethylene was converted to C_3 and C_4 hydrocarbons. The same zeolites behaved quite differently when partially dehydroxylated. Polymerization was rapid and the retained residues now became sites for the reaction. In agreement with earlier work with silica–alumina catalysts (*1–3*), these prevented the exchange reaction from being studied. Recently, Ward (*30*) has summarized evidence concerning the enhancement of the intrinsic strength of the Bronsted sites by dehydroxylation or by substitution of multivalent cations. The reaction coordinate is therefore very significantly altered by pretreatment. It is fruitful to speculate that the metastable potential well corresponding to the carbonium ion may become very shallow for catalysts treated as required for our experiments, i.e., the lifetime of the carbonium ion becomes very short and fades into a transition state for exchange. In this way polymerization is uncoupled from the exchange. These ideas are supported by the effects observed (*15*) when C_3H_6 is substituted for C_2H_4 over these same surfaces.

One of the objectives of this work was to determine the activation energy for the exchange reaction and to associate it with that for carbonium ion formation. Since the rate of the exchange reaction was first order in C_2D_4 pressure, its true activation energy should be the sum of the apparent activation energy and the heat of adsorption. Thus, the value derived could not be more than $19 + 9 = 28$ kcal/mole. This value appears too low for the formation of a primary carbonium ion. Reactions involving secondary carbonium ions have apparent activation energies in the range 10–15 kcal/mole and heats of adsorption at least as great as that for ethylene. Thus, the true activation energies for these reactions would reasonably exceed 20 kcal/mole. It is usually supposed that the energy of a primary ion is higher than that of a secondary ion by at least 15 kcal/mole.

It has been and remains our opinion that the act of proton transfer in carbonium ion formation involves tunneling of the proton from the Bronsted site onto the unsaturated hydrocarbon via a strong charge-transfer complex, and that the ease of transfer parallels the strength of the hydrogen bond. The hopping of hydrogen from oxygen to oxygen, as shown by the NMR results, probably involves a similar process. The present work demonstrates some of the difficulties which arise when attempts are made to apply physical techniques quantitatively to kinetic problems. Unexpected complications occur which obscure the information sought.

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