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The Role of the Proton in the Catalytic Cracking of Hexane Using a Zeolite Catalyst

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The catalytic cracking activity of zeolite catalysts has been attributed to the existence of protons present in the zeolite framework as hydroxyl groups. The present study shows that the gradual deactivation of the catalyst is accompanied by the progressive removal of hydroxyl groups as determined by infrared analysis. Complete removal of hydroxyl groups coincides with the loss in catalytic cracking activity. The cracking of hexane was carried out using a deamminated, ammonium-exchanged Type Y molecular sieve, having a SiO_2–Al_2O_3 ratio of 5. The cracking reaction causes the removal of first the 3640 cm^{-1} absorption band in the hydroxyl stretching region and subsequently the 3540 cm^{-1} band. The loss of the former band is characterized by a change in the product selectivity from C_3 and C_4 hydrocarbons to principally C_1 and C_2 hydrocarbons. The release of hydroxyl hydrogens from the zeolite would satisfactorily account for the high paraffin to olefin ratios reported in the literature for the products obtained from the cracking of paraffins over zeolite catalysts.

INTRODUCTION

The advent of zeolite-containing cracking catalysts in the Petroleum Industry brought about a marked change in the selectivity of the cracked product. It is well established that the principal differences observed between zeolite-containing catalysts and the conventional amorphous silica–alumina catalysts are that the former (1) are significantly more active, (2) produce less C_1 and C_2 hydrocarbons, (3) produce less olefins, and (4) have a considerably lower coke formation. Numerous studies have been reported on the nature of catalytic cracking with zeolites and have attempted to explain the high activity and improved selectivity induced by the zeolite component (*1–7*). The principal controversy about the mechanism of zeolite catalysis concerns the role of the proton. Some investigators choose to explain the catalytic activity of a deamminated, ammonium-exchanged zeolite by a polarization mechanism (*3*) or by the related dynamic (time variant) concept arising from the surface diffusion of oxide ions (*5*). Other investigators, however, prefer the classical Brönsted acid mechanism (*6, 7*) or one involving combined Brönsted–Lewis acidity (*4*). The experimental evidence in favor of the Brönsted acid mechanism would seem substantial since the catalytic activity of a deamminated, ammonium-exchanged Y is observed when protons, present as hydroxyl groups, are known to be present and zero activity is observed when the zeolite has been completely dehydroxylated (*2*). However, maximum activity is not observed when the proton content of the zeolite is at its maximum, after calcination at 380°C when the deammination step is complete for a 95% ammonium-exchanged Y, but at a 150°C higher calcination temperature (*2, 8*). Thus, although it is not unambiguously established that the proton is the active site, it is known that catalytic cracking is associated with its presence.

The generally accepted mechanism of catalytic cracking involves the classical carbonium ion intermediate. However, the products predicted by this carbonium ion mechanism are not consistent with experimental data obtained using zeolite catalysts. This theory, in the case of hexane cracking, requires a paraffin-to-olefin ratio of unity as well as at least an equal amount of C_2 hydrocarbon to account for the formation of the C_4 hydrocarbons found experimentally. Benesi has reported that all the products obtained from the cracking of *n*-butane and *n*-pentane over a mordenite catalyst at 400°C are paraffins; no olefins are formed (*1*). Weisz *et al.* have shown that the products obtained from the cracking of *n*-pentane and *n*-hexane at 232°C are saturated C_3 and C_4 hydrocarbons; virtually no C_1 or C_2 hydrocarbons are formed (*9*). These and other studies by Tung and McIninch (*5*) have established that below a reaction temperature of approximately 300°C, the products from the catalytic cracking of hexane using a zeolite catalyst are principally saturated C_3 and C_4 hydrocarbons which is not consistent with a simple cleavage of the carbonium ion intermediate. Higher reaction temperatures result in increasing amounts of unsaturates and C_1 and C_2 hydrocarbons. The different product selectivities exhibited at the different ranges may be explained either by the desorption of preferentially adsorbed unsaturates by the higher temperatures or that two cracking mechanisms are operative, one at the lower temperature range and the other at the higher temperature range.

A close examination of the analyses of the cracked products obtained by Tung and McIninch indicate that a correlation may well exist between the nature of the catalyst and the product selectivity (*5*). Their studies showed that at a particular reaction temperature, the saturate-to-unsaturate ratio increases with increasing sodium removal. Increasing sodium removal, i.e., increasing extents of ammonium exchange will result, after activation, in increasing hydroxyl content. This might indicate that the proton, present as an hydroxyl group, may well play another role, other than that of the primary active site. Since the stoichiometry of the cracking reactions requires a paraffin to yield at least as much olefin as paraffin, a source of hydrogen is required. It is generally accepted that the hydrogen is derived by hydrogen-transfer reactions during coke formation on the catalyst. However, it could well be that the hydroxyl groups present on the zeolite are also a source of the hydrogen required to saturate the olefin portion of the cracked products. Support for this hypothesis may be provided by the work of Eberly who found that hexene-1 loses its characteristic olefinic stretching frequency when adsorbed on deamminated Y and that preferential interaction with the hydroxyl group at 3640 cm^{-1} occurs (*10*). Some preliminary observations by Ward showed that, during cumene cracking over deamminated Y at 250°C, the intensity of the hydroxyl groups at 3640 cm^{-1} continuously decreases (*11*). Ward interpreted these data as the interaction of cumene with the hydroxyl groups, but the consumption of hydrogen from the hydroxyl group by propylene could also be a satisfactory explanation especially as propane and not propylene is produced initially under these conditions (*12*).

This study was concerned with observing by infrared analysis, the effects of the catalytic cracking reaction on the hydroxyl groups of deamminated, ammonium-exchanged Y zeolite and correlating these effects with changes in the distribution of the cracked products.

EXPERIMENTAL

Materials

The samples used in this study were prepared from pure Type Y molecular sieve synthesized by Linde. The ammonium-exchanged forms were prepared by repeatedly contacting the zeolite powder with a 10% aqueous solution of ammonium chloride at reflux temperatures. The products were washed with demineralized water until free of chloride ions and dried in ambient air.

Infrared Analysis

The samples were run as self-supporting wafers and scanned on a Perkin–Elmer 621 spectrophotometer from 3800 to 3400 cm^{-1}. The wafers had weights of approximately 6 mg/cm^2 and were formed by pressing about 30 mg of powder in a 1 in.-diameter die to a pressure of 4000 psig. The wafers were placed in a cell similar to that described by Angell and Shaffer but modified to allow for the flow of an hydrocarbon over the wafer, and calcined at 550°C for 2.5 hr with a 2 ft^3/hr air purge (*13*). After calcination the cell was purged with nitrogen for 1 hr at 550°C. The spectrum of the wafer was then obtained under anhydrous conditions after the cell was cooled to room temperature. The cell was then heated to 450°C, and *n*-hexane in nitrogen was passed through the cell. Gas samples of the product were analyzed by chromatography periodically. After 1 hr the cell was cooled to 200°C and evacuated to remove *n*-hexane and other condensed hydrocarbons. It was then cooled to room temperature and the spectrum of the wafer obtained under anhydrous conditions. The

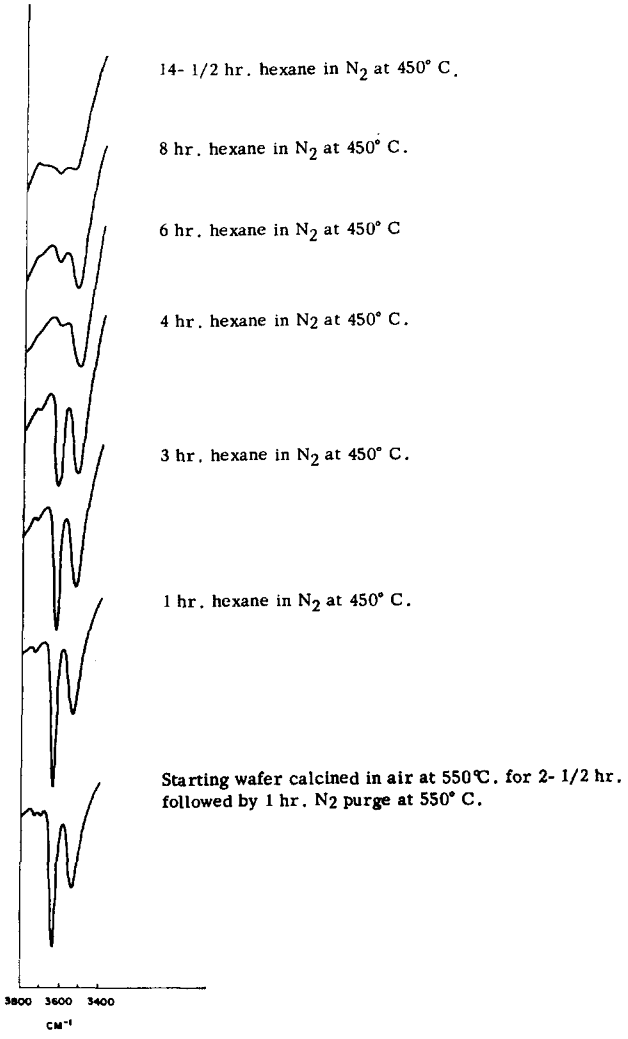

Fig. 1. Infrared spectra of hydroxyl region of deamminated NH$_4$Y after hexane cracking. Spectra obtained at room temperature under anhydrous conditions.

cell was next filled with nitrogen, heated to 450°C and *n*-hexane in nitrogen passed over the wafer again. The cell construction was such that only a portion of the available hexane came into contact with the zeolite wafer and thus determinations of hydrocarbon conversion could not be made.

RESULTS

The infrared spectra of the hydroxyl stretching region of a deamminated, 73% ammonium-exchanged Y after being used for the cracking of *n*-hexane at 450°C are presented in Fig. 1. This figure shows that the 3640 cm^{-1} band is selectively and progressively removed by the catalytic cracking reaction. The 3540 cm^{-1} band remains constant in intensity until the 3640 cm^{-1} band is reduced to below approximately 20% of its original intensity when it too begins to decrease. That the disappearance of the hydroxyl bands was not a result of either temperature or vacuum treatments undergone during the cracking and the subsequent infrared analyses was shown by subjecting the zeolite wafers to the same cycling treatments. No diminution in intensities of the 3640 or 3540 cm^{-1} bands were observed.

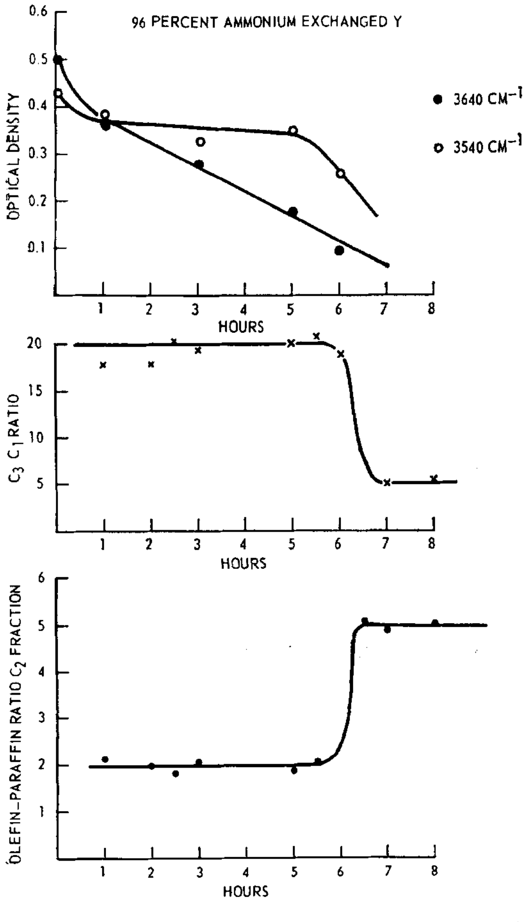

FIG. 2. Catalytic cracking at 450°C using a 96% ammonium-exchanged Y.

The chromatographic analysis of the cracked product was determined as a function of reaction time for three different zeolite samples having different levels of original ammonium exchange. These data are shown in Figs. 2, 3, and 4. The decrease in intensity of the 3640 cm^{-1} band is shown to be a linear function of the reaction time. Initially, the products are principally C_3 and C_4 saturated hydrocarbons but change abruptly to C_1 and C_2 hydrocarbons when the intensity of the 3640 cm^{-1} band is reduced by about 80% of its original value. At 450°, the initial C_3-to-C_1 ratio varies with percentage of original ammonium exchange, from approximately 20 for a 96% exchanged material to 5 for a 39% exchanged material. Coincidental with the change in the C_3-to-C_1 ratio, is a variation in the olefin-to-paraffin ratio of the C_2 hydrocarbons from between 2 and 3 depending on the degree of original ammonium exchange, to approximately 5. Analyses of the products from an experiment carried out at 450°C in the absence of a zeolite wafer, show the infrared cell and wafer holder to promote a small amount of cracked product. These data, given in Fig. 5, show the C_3-to-C_1 ratio and the C_2 olefin-to-paraffin ratio to be approximately 2.5 and 4.5, respectively. These values are characteristic of the product obtained in the presence of the zeolite, but only after the 3640 cm^{-1} band has been reduced to below 20% of its original intensity, Fig. 5. The regeneration of these catalysts by treatment at 450°C in air did not result in the reconstitution of the hydroxyl groups nor in the restoration of catalytic selectivity to their original values. The cracking of *n*-hexane over a deamminated, 96% ammonium-exchanged Y at 350°C pro-

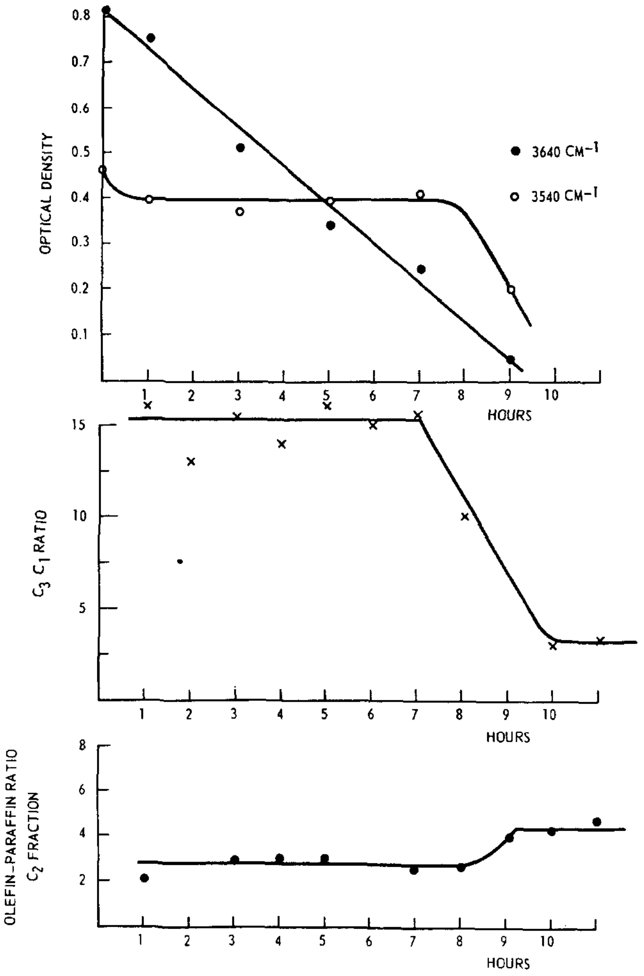

Fig. 3. Catalytic cracking at 450°C using a 73% ammonium-exchanged Y.

duced an initially completely saturated product and a C_3-to-C_1 ratio of approximately 60 as compared to a value of 20 obtained at 450°C, Fig. 6. The substitution of hydrogen for nitrogen as the hexane carrier did not produce any changes in the rate of disappearance of the 3640 cm^{-1} band nor in the selectivity of the cracked product. The incorporation of palladium onto the zeolite together with the use of hydrogen instead of nitrogen as the hexane carrier produced the same C_3-to-C_1 hydrocarbon ratio as the nonmetal loaded zeolite, yielded no unsaturated hydrocarbons and did not result in the disappearance of either the 3640 cm^{-1} band nor the 3540 cm^{-1} band. These data are shown in Fig. 7.

Discussion

An examination should first be given to the results obtained in this and previous studies on the nature of the cracked products and their variation with catalyst composition and reaction temperature. It was previously pointed out that a catalytic cracking mechanism postulating a simple cleavage of a carbon–carbon bond does not explain the experimental data derived from the cracking of *n*-hexane over zeolite catalysts. At temperatures below about 350°C, virtually no C_1 and C_2 hydrocarbons are formed to account for the presence of C_4 and C_5 hydrocarbons and the absence of unsaturated product requires an explana-

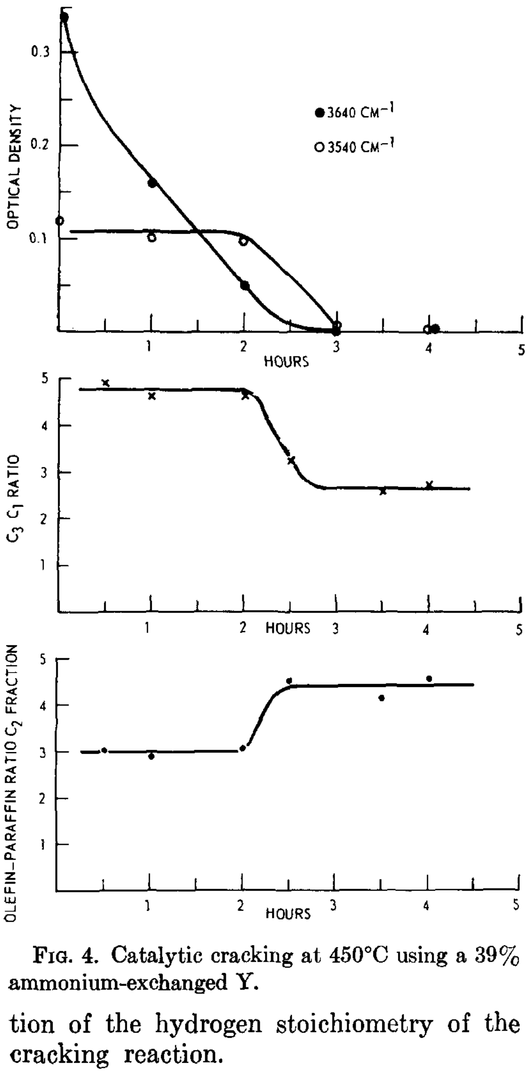

Fig. 4. Catalytic cracking at 450°C using a 39% ammonium-exchanged Y.

tion of the hydrogen stoichiometry of the cracking reaction.

A cracking mechanism via disproportionation, previously used to explain the isomerization of the hexane isomers, partially explains the observed product selectivity at the lower reaction temperatures (*14*).

$$\begin{aligned} 2\,nC_6 \rightarrow [C_{12}] &\rightarrow 3\,C_4 \\ &\rightarrow 4\,C_3 \\ &\rightarrow C_3 + C_4 + C_5 \end{aligned}$$

Probably all three of these reactions occur simultaneously to varying degrees. The products from the catalytic cracking of *n*-pentane and *n*-butane which have been reported to be C_3 and C_4 hydrocarbons and C_3 and C_5 hydrocarbons, respectively, are also successfully predicted by a disproportionation mechanism (*9*).

$$2\,nC_5 \rightarrow [C_{10}] \rightarrow C_4 + 2\,C_3$$
$$2\,nC_4 \rightarrow [C_8] \rightarrow C_3 + C_5$$

This mechanism also accounts for the occurrence of products having a higher carbon number than the reactant molecule.

Although a cracking mechanism via disproportionation allows the paraffin–olefin ratio to be as high as 2 for the products of hexane cracking, it does not account for the virtual absence of olefins from the products obtained at temperatures below 350°C (*1, 9*). It is generally accepted that the hydrogen required to saturate the olefin is derived from aromatic and coke formation. However, at temperatures below 350°C, aromatic formation is too low to make a significant contribution. The principal differences between zeolites and amorphous silica–alumina cracking catalysts is that less olefins are produced at significantly reduced coke levels. Thus hydrogen-transfer reactions via coke formation cannot be the principal source of the hydrogen required to saturate the cracked product. It has never been clearly established whether coke formation is the cause of loss in catalytic activity or if coke is formed as a result of a decline in catalytic activity. The other possible source of hydrogen required to satisfy the stoichiometry of the reaction is the catalyst itself. Thus catalytic cracking is envisaged to take place in two steps; the primary cracking reaction occurring at the sites formed by dehydroxylation followed by the saturation of the olefin by hydrogen derived from the hydroxyl groups.

The data obtained from the infrared study of the catalyst during the catalytic cracking reaction support this theory. The disappearance of the hydroxyl group at 3640 cm^{-1} in the hydroxyl stretching region of the infrared spectrum of the zeolite is evidence that during the catalytic cracking reaction, the catalyst is undergoing a significant change (Fig. 1). The data in Figs. 2, 3, and 4 show that the 3640 cm^{-1} band decreases linearly with time on stream indicating that the hydroxyl loss is associated with the cracking reaction. Although no quantitative estimations of coke formation were made, it was observed

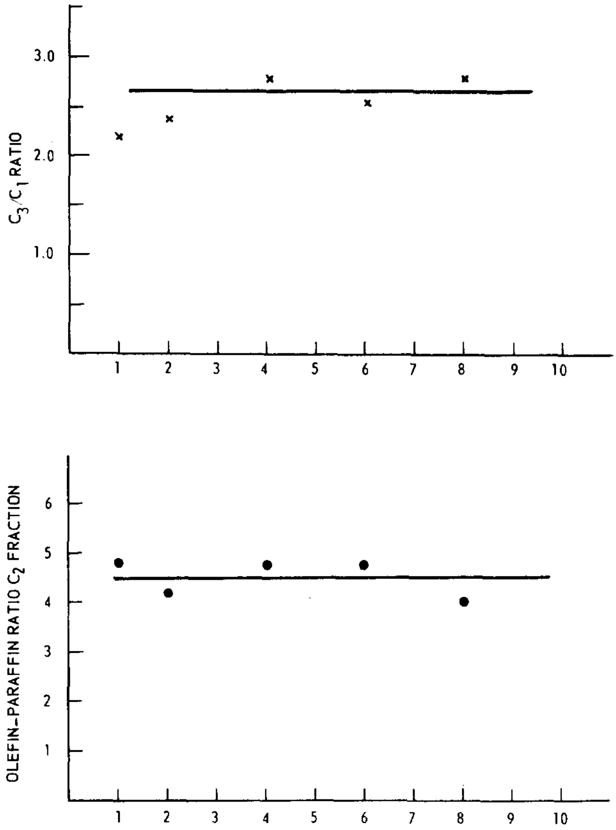

FIG. 5. Thermal cracking at 450°C in infrared cell and in absence of zeolite.

from the color and optical transmittance of the zeolite wafers that little coke formation takes place while at least 20% of the original intensity is present. After the intensity of this band was reduced below this value, the wafer rapidly became opaque and turned black. Coincidental with the reduction of the 3640 cm^{-1} band to 20% of its original intensity was a change in product distribution from a typical ionic type distribution to that characteristic of thermal cracking and identical to that taking place in the infrared cell and wafer holder and in the absence of the zeolite. That the observed olefin–paraffin ratios of the C_2 hydrocarbons are higher than unity was unexpected. However, stochiometry only requires the overall olefin–paraffin ratios of the cracked product to be no higher than unity and these high ratios were found to be adequately counterbalanced by the significantly lower olefin–paraffin ratios of the C_3 and C_4 hydrocarbons. The product distributions shown in Figs, 2, 3, and 4 are in agreement with the published studies of Tung and McIninch (*5*). Increasing degrees of ammonium exchange result in catalysts producing increasing C_3-to-C_1 ratios and decreasing C_2 unsaturate-to-saturate ratios. The higher the extent of original ammonium exchange, the higher the concentration of hydroxyl groups in the activated catalyst. This is not to imply that the proton, present as a hydroxyl group, is the active site since it has previously been pointed out that maximum cracking activity occurs after a substantial amount of dehydroxylation takes place. A satisfactory explanation is that the active site is something other than the proton, but the rate-determining step of the reaction is the desorption of olefin from the zeolite. Thus desorption is facilitated by an hydrogen

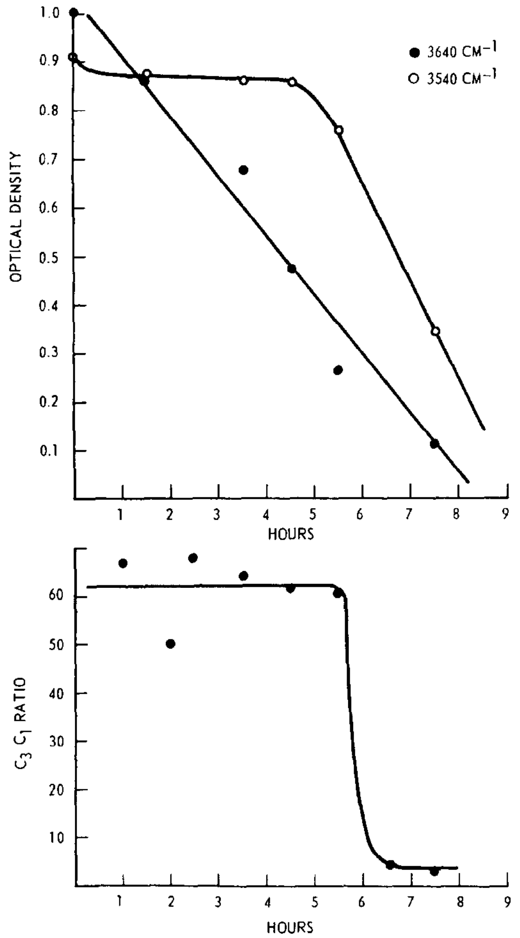

FIG. 6. Catalytic cracking at 350°C using a 96% ammonium-exchanged Y.

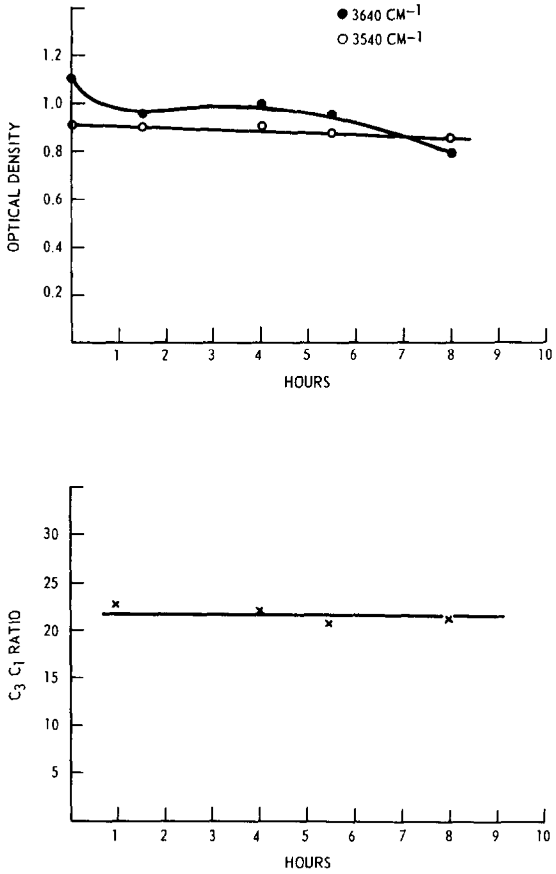

FIG. 7. Cracking in the presence of hydrogen at 450°C using a palladium-loaded 96% ammonium-exchanged Y.

transfer from the hydroxyl group to the olefin. Such an explanation would account for the increasing cracking activity with an increasing amount of original ammonium exchange. The change in product distribution that is observed when the reaction temperature is reduced from 450 to 350°C, Fig. 5, is in accord with the published studies of Weisz *et al.* (*9*). The lower temperature brings about a higher C_3-to-C_1 ratio together with the elimination of olefin formation.

It is suggested that the results of this and other studies indicate that catalytic cracking of paraffins takes place by two reactions, one of which is monomolecular and involves direct scission of a carbon–carbon bond and another which is a disproportionation reaction. That a significant amount of the product is derived from a disproportionation reaction and not by fragmentation and subsequent recombination is confirmed by the same C_3-to-C_1 ratio being observed under conditions which would result in at least the partial hydrogenation of the fragmentation products. This is shown by a comparison of the results in Figs. 2 and 7. The variation in selectivity exhibited by different catalysts may well be a function of the extent to which each of these two reactions proceeds. Data from previous studies (*5, 9*) together with Figs. 2 and 6 would show that the relative contributions of these two reactions is a function of the reaction temperature. At temperatures of approximately 350°C and below, the products would indicate that the reaction is principally of a disproportionation type but the products from higher reaction temperatures would show that the reaction proceeds by both mechanisms. The occurrence of increasing amounts of olefins in the reaction products with increasing temperature may also be a result of increasing ease of olefin desorption before hydrogen-transfer reactions have taken place. The rapid reduction in intensity of the 3540 cm^{-1} band after the 3640 cm^{-1} band has been substantially removed by the cracking reaction is not understood. The coincidental loss of transmittance and coke deposition on the zeolite wafer are thought to be related to the reduction in intensity of this band.

The incorporation of an hydrogenation component onto the zeolite together with the use of hydrogen as the carrier gas shows the hydroxyl groups to be relatively unaffected by the hydrocracking reaction. The explanation of these data is either that the hydrogenation of the olefins by the palladium obviates the need for the hydrogen-transfer reactions or that the palladium is absorbing molecular hydrogen and subsequently protonating the zeolite as rapidly as the hydrogen-transfer reactions deplete the zeolite of hydrogen atoms. The latter possibility is suggested by the reaction of noble metal-loaded zeolites with hydrogen (15). The reconstitution of the 3640 cm^{-1} band, reduced by hexane cracking in a nitrogen purge, on a palladium-loaded deamminated Y by an hydrogen treatment was unsuccessfully attempted. It is possible that high hydrogen partial pressures, typical hydrocracking conditions, are required to achieve this reconstitution.

Support for the proposal that hydrogen is derived from the catalyst is provided by a critical experiment reported in a study by Tung and McIninch (*5*). They observed, in agreement with this study, that the recalcination of a deactivated catalyst in air at 550°C did not restore catalytic activity. It was logically concluded that deactivation could not be attributed to coke formation and it was proposed that surface reconstitution, brought about by the hexane feed, had taken place. If, however, the hydrogen content of the catalyst is reduced by olefin saturation, no further activity could be expected since recalcination in air at 550°C, even in the presence of water derived from the coke burn-off, cannot be expected to reconstitute hydroxyl groups (*14*). The explanation of these data must be the same as that required to account for the lack of activity of completely dehydroxylated Y; that catalytic cracking cannot occur in the absence of available hydrogen required to saturated the strongly absorbed olefin and remove it from the active site.

Additional experimental data must be obtained, including an exact determination of the hydrogen balance during the course of the cracking reaction to corroborate this concept.

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