NOTES

The Effect of Hydrogen on the Adsorption and Reaction of 1-Hexene over HY Cracking Catalysts

In situ Fourier transform infrared spectroscopy was used to study the reaction of 1-hexene over HY catalysts at temperatures from 200 to 400°C. The addition of hydrogen to the reaction mixture altered the adsorption of 1-hexene, leaving the double bond intact and inhibiting hydrocarbon transformations and coke formation. Adsorption was much greater when hydrogen was present. When hydrogen was omitted, the adsorbed species showed signs of transforming to branched compounds. The absence of adsorbed aromatics led to the suggestion that coke formation proceeded through a polymerization–isomerization–dehydrogenation reaction sequence.

INTRODUCTION

The catalytic cracking of hydrocarbons over acidic zeolite catalysts has been an intriguing problem for scientists and engineers for many years. Economically one of the most important processes in the world today, catalytic cracking is still far from being fundamentally understood. At the heart of the problem is the fact that the mechanisms of cracking reactions and the nature of adsorbed species on zeolites are not well understood.

In an earlier study (1), *in situ* Fourier transform infrared (FTIR) spectroscopy was applied to the study of the nature of the active sites for HY catalysts in different cracking reactions. In the present study, this technique was used to investigate the adsorption and reaction of 1-hexene on HY cracking catalysts, in the presence and absence of hydrogen in the reaction stream.

EXPERIMENTAL

The catalyst, reagents, infrared cell, and spectrometer used in this study have been described previously (1). Samples were calcined in flowing oxygen and helium for 1 h to remove water and ammonia. The cell was then cooled to 200°C to begin the reaction. During reaction, the temperature was raised in steps of 100°C to 400°C. At each step, the reaction was allowed to proceed for more than 30 min. Spectra were re-

corded every 15 min. The figures in this paper represent the catalyst after 30 min under isothermal conditions, a time at which no further changes could be noted in the spectra. This stepwise temperature progression permitted a study of the differences in adsorbed species at different (but constant) reaction temperatures. Each experiment was replicated at least once, with consistent results.

RESULTS

The calcined HY samples exhibited a large concentration of supercage hydroxyl groups (1). These hydroxyl groups were quickly consumed and the peak was severely diminished after less than 15 min at 200°C with 1-hexene, in the presence or absence of hydrogen. Therefore, supercage hydroxyl groups did not play a role in the reactions studied here.

Adsorption of 1-hexene on HY resulted in much more intense spectral features in the presence of hydrogen at every temperature. The aliphatic stretching region between 2800 and 3000 cm^{-1} shows strong absorbance (greater than 3 absorbance units) in the IR spectra, indicating that the concentration of adsorbed aliphatic hydrocarbons is very large when hydrogen is present in the reactant stream. Spectra recorded of the gas phase alone, after removal of the sample wafer from the beam path, show that some, but not all, of the IR absorbance

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is due to gaseous 1-hexene. A substantial part of the hydrocarbon peak seen in this region is associated with the catalyst, either physically trapped in the pores, or adsorbed on the catalyst surface.

The hydrocarbon deformation region peaks observed are not due to gaseous hydrocarbons, and, since they undergo changes as the reaction temperature is changed, they are attributed to adsorbed hydrocarbon species.

200°C

In Fig. 1, some very important differences are evident in the spectra of 1-hexene on HY in the presence and absence of hydrogen. With hydrogen in the reactant stream (Fig. 1A), the 1-hexene spectra resembled those of gaseous 1-hexene in position and relative intensity of the IR peaks. Spectra of the cell with the sample holder removed showed that little of the infrared absorption was due to gas-phase species. Prominent peaks near 3100 and 1640 cm^{-1} indicate that the double-bond character of the 1-hexene remains intact. The only substantial difference from the gaseous spectra is the presence of a peak at 1585 cm^{-1}, which has been previously assigned to the formation of complex carbonaceous deposits on the surface (2, 3). This peak appears in the spectrum concomitant with the decrease of the 3640-cm^{-1} supercage OH peak, and this relationship is discussed in another paper (1).
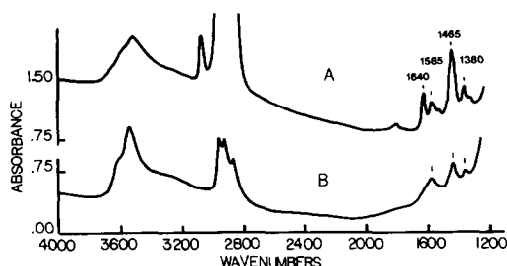

FIG. 1. FTIR spectra after 30 min of 1-hexene reaction at 200°C over HY catalyst calcined at 400°C. (A) H$_2$ added to the reaction stream. (B) H$_2$ omitted from the reaction stream.
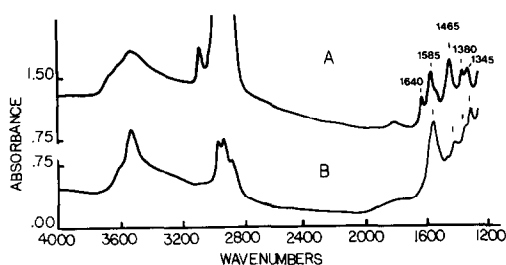

FIG. 2. FTIR spectra after 30 min of 1-hexene reaction at 300°C over HY catalyst calcined at 400°C. (A) H$_2$ added to the reaction stream. (B) H$_2$ omitted from the reaction stream.

When hydrogen is omitted from the reaction stream (Fig. 1B), the hydrocarbon adsorption peaks show a substantial change. No peak is observed at 1640 cm^{-1}, and the peak at 3100 cm^{-1} is extremely small and probably is due to a slight amount of gaseous 1-hexene present in the cell. This indicates that the adsorbed species no longer retains the terminal double bond. Other adsorption peaks in the deformation region are similar to, though less intense than, those in the spectrum of the sample with hydrogen. These include the "umbrella" CH$_3$ peak at 1380 cm^{-1} and the –CH$_2$ peak at 1465 cm^{-1}.

300°C

More changes in hydrocarbon adsorption are evident in Fig. 2 for both the sample with hydrogen and the one without hydrogen. The double-bond character of the adsorbed species is still evident for the sample in which hydrogen was present, although the growth of the coke peak has begun to interfere with the peak at 1640 cm^{-1}.

The hydrocarbon peaks in the deformation region have undergone some changes with the increase in temperature, especially for the sample in which no hydrogen was used (Fig. 2B). With no hydrogen in the reactant stream, the prominent peak at 1465 cm^{-1} which represented methyl and methylene group bending vibrations decreases and shifts to lower frequency. The "um-

brella" CH_3 peak at 1380 cm^{-1} is now a shoulder on a large, dominant peak at 1340 cm^{-1}. This new peak represents a –CH bond of a tertiary carbon, indicating that branching of the linear hydrocarbon reactant may be taking place. The coke peak is considerably larger than when H_2 is present.

When H_2 is added to the reactant stream, the changes in the hydrocarbon deformation region of the spectrum discussed above are not as prominent, as seen in Fig. 2A. The peak at 1465 cm^{-1} is still the most dominant one and has not shifted to lower frequency. The new 1340-cm^{-1} peak is separate from the 1380-cm^{-1} peak. Evidently the adsorbed hydrocarbon retains more of its original form as temperature is increased if H_2 has been added to the reactant stream.

400°C

The hydrocarbon region from 1300 to 1600 cm^{-1} is shown in the right part of Fig. 3. The coke peak has grown considerably in both cases, but is still greater in the absence of H_2. For Fig. 3A, the sample with hydrogen, the peak at 1640 cm^{-1} representing the terminal double bond has become a shoulder on the coke peak. A band at 3100 cm^{-1} is still present but has diminished in intensity.

The tertiary –CH peak at 1340 cm^{-1} is growing relative to the other hydrocarbon peaks for both samples, indicating that with

increased contact and higher temperature the alteration of the 1-hexene reactant continues, possibly involving polymerization of 1-hexene to form a branched aliphatic polymer.

At none of the temperatures under study was a substantial amount of absorption due to aromatic species observed. The nature of the species represented by the peak at 1585 cm^{-1} is still ill defined and may involve highly dehydrogenated C=C compounds or aromatic or cyclic skeletal structures. No peaks near 1500 cm^{-1} or above 3000 cm^{-1} were observed to support the assertion of aromaticity of the adsorbed surface species. However, the aromatic regions below 1200 cm^{-1} were obscured due to vibrations of the zeolite structure.

DISCUSSION

The most striking difference between the reactions with and without H_2 lies in the double-bond character of the adsorption of 1-hexene in the presence of H_2. In Eberly's (*4*) IR work involving adsorption of the same compound on a similar catalyst, the double bond of 1-hexene was lost even with adsorption at temperatures as low as 93°C; however, no H_2 was used in these experiments. Eisenbach and Gallei (*3*) also used 1-hexene in an IR study; they observed the C=CH$_2$ peak at 1640 cm^{-1} up to 257°C on a Pt—CaY catalyst, and H_2 was used in the reactant stream. In another study involving propylene (*5*), no H_2 was used in the reaction and no such double-bond character was observed. It seems from these results and those of the present study that hydrogen has the effect of inhibiting strong chemisorption of olefins at the double bond; the C=C bond is still present, a carbonium ion has more difficulty in forming, and the compound is probably only weakly associated with the catalyst.

This weak association must account for only a part of the adsorbed 1-hexene. As shown in Fig. 1, the supercage hydroxyl groups are being consumed at 200°C, and
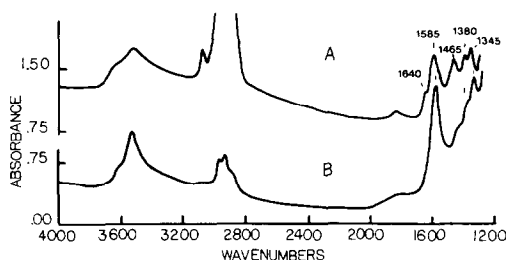

Fig. 3. FTIR spectra after 30 min of 1-hexene reaction at 400°C over HY catalyst calcined at 400°C. (A) H_2 added to the reaction stream. (B) H_2 omitted from the reaction stream.

the coke peak is also growing at this temperature. It is unlikely that the depletion of a catalyst's active sites and the growth of a complex carbonaceous surface species occur merely through weak association with a hydrocarbon which retains its gaseous structure. (For reactions other than cracking, however, suggestions of weak acid sites being involved in coke formation have been made (6)). Apparently only a certain percentage of the adsorption involves the weaker interaction which preserves the double bond, while the remaining adsorption is strong enough to react with hydroxyl groups and to produce coke.

The nature of this weak association of the 1-hexene is still undefined. Several possible suggestions are offered at present: the association might involve some weak interaction such as hydrogen bonding between the hydrocarbon and the zeolitic hydroxyl group, or it might interact directly with adsorbed hydrocarbons, coke, or coke precursors on the surface. The coke itself has been suggested to be an active site in cracking reactions (7).

Another suggestion is that, in the presence of hydrogen, the 1-hexene preferentially remains trapped within the pores rather than undergoing the stronger interaction involved in adsorption. Calculations have shown (8) that diffusion of olefins out of zeolite pores is inhibited by electrostatic interaction between the zeolite lattice and the olefinic pi bonds. If hydrogen keeps the olefin from strong interaction with the catalyst's active sites, and the zeolite keeps the olefin from quickly diffusing out of the supercages, the result might be a large concentration of 1-hexene within the zeolite pores, involved in a weak interaction with the zeolite. This would also account for the higher intensity of hydrocarbon peaks observed in the spectra of samples with H_2 included in the reactant stream. This suggests that for samples with no hydrogen present, the 1-hexene undergoes reaction with the active sites more rapidly and hence does not remain in the supercages

with the same weak association with the zeolite.

The presence of hydrogen in the reactant stream appears to inhibit the rearrangement of the adsorbed 1-hexene reactant. At lower temperatures the adsorbed hydrocarbon peaks in the deformation regions show that the 1-hexene has not rearranged to a great extent on the surface. Only at the highest temperature did the branching of the linear hydrocarbon occur. This behavior of hydrogen in inhibiting transformations is not unexpected. The cracking reaction products may be supplied with hydrogen from the gas phase rather than with hydrogen abstracted from the adsorbed species. Without this abstraction, the surface hydrocarbons remain intact for a longer period of time. This might also account for the smaller coke peak intensity for spectra taken of the reaction in the presence of H_2.

When no hydrogen is used in the reactant stream, rearrangement occurs rapidly. The tertiary CH peak grows concomitant with the coke peak, and the dominant $-CH_2$ or CH_3 bending peak at 1465 cm^{-1} is diminished and shifted, indicating that the molecule has undergone transformation on the surface. Eisenbach and Gallei (3) attribute these changes to the formation of a tertiary carbonium ion on the zeolite surface. Another possible suggestion is that the surface carbonium ion that is formed becomes an active site for further adsorption, triggering the formation of a highly branched polymeric surface species that may be a precursor to coke. The lack of detectable adsorbed aromatic species also hints at some type of polymerization–dehydrogenation reaction sequence leading to coke formation.

The IR peak attributed to coke has been observed previously, but the chemical nature of the coke deposits has not been clearly defined. In addition to IR studies, work involving X-ray diffraction and electron microscopy has found the coke to consist of some highly dehydrogenated spe-

cies, possibly dienic or graphitic in nature (9). Even less certain is the nature of the precursors to this coke species, the most likely candidates being adsorbed aromatics or conjugated dienic compounds. The lack of aromatic IR peaks in the spectra, and the presence of branched aliphatic peaks, suggest that coke may form from 1-hexene without first aromatizing or forming ring structures.

The fact that aromatic compounds were not observed to form on the catalyst surface deserves further discussion. Nearly all previous investigations devoted to coke formation on cracking catalysts have assumed or found evidence for aromatics as the predominant contributors to coke. Techniques used in these studies include extraction of the coke deposits from the catalyst and gas chromatographic and/or mass spectroscopic analysis of the extracted material. These procedures have a major drawback in that they involve chemical treatment or extraction of the coke before analysis, opening the possibility of postreaction modification of the coke composition, or selective removal of constituents. One important advantage of FTIR is in its real-time, undestructive analysis of the catalyst sample. *In situ* FTIR spectroscopy offers the possibility of monitoring a chemical reaction as it is taking place. This technique would seem to provide an accurate picture of the catalyst surface during the reaction. The fact that no aromatics were observed in the expected regions of the spectrum during the reaction with 1-hexene leads to the speculation that a mechanism for coke formation may proceed through intermediates other than aromatic compounds. The indications of branching of the adsorbed hydrocarbons mentioned earlier then become an even stronger piece of evidence for this conclusion. If aromatics are indeed coke precursors, they must become dehydrogenated so rapidly that –CH– linkages are not observed, or they must exist in a configuration in which their IR absorbance is attenuated.

CONCLUSIONS

Reactions of 1-hexene over HY cracking catalysts were observed by *in situ* FTIR spectroscopy at temperatures between 200 and 400°C. Reactions in which hydrogen was mixed in the reactant stream showed that at least some of the hydrocarbon was adsorbed in a manner that retained the terminal double-bond character of the reactant. Hydrocarbon modification and formation of coke were inhibited at lower temperatures with hydrogen in the reactant stream. The concentration of hydrocarbon on or associated with the catalyst surface was much greater in the presence of hydrogen.

When hydrogen was omitted from the reaction, the double bond of the 1-hexene was lost upon adsorption, suggesting a carbonium ion mechanism in the adsorption of the reactant. Coke formation proceeded concomitant with hydrocarbon transformations on the surface that indicated branching of the linear compound. A distinct lack of adsorbed aromatic compounds was noted both in the presence and absence of hydrogen, leading to the postulation of a polymerization–dehydrogenation reaction sequence for the formation of coke.

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