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In Situ Fourier Transform Infrared Spectroscopy Study of HY Cracking Catalysts: Coke Formation and the Nature of the Active Sites

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An *in situ* Fourier transform infrared spectroscopic investigation of coke formation on HY cracking catalysts was undertaken using NH_4Y catalysts calcined between 300 and 538°C, with 1-hexene and 4-methylcyclohexene used separately as reactants. Two types of active sites are proposed for the formation of coke. One site consists of the Brønsted acid hydroxyl groups present after low-temperature calcination. The second type of site involves a sort of synergism between stronger Brønsted acid hydroxyl groups and neighboring Lewis acid cationic sites, formed after high-temperature calcination. This dual-site suggestion for coking parallels similar suggestions made previously for cracking reactions on these catalysts. The composition of the coke on the catalysts exhibited a distinct lack of aromatic character, suggesting that the route to coke formation need not always proceed through aromatic precursors.

INTRODUCTION

The catalytic cracking of long-chain hydrocarbons into smaller molecules is invariably accompanied by the formation of coke deposits on the catalyst surface. The term coke may refer to any high-molecular-weight, highly carbonaceous species that is deposited on the catalyst surface. While the chemical nature of these deposits is not completely understood, their effect on catalyst activity is well known. Coking causes catalyst deactivation either by blockage or poisoning of the catalyst's active sites.

In order to address the problem of zeolite catalyst deactivation by coking, the chemical identity and origin of the coke deposits must be better understood. This entails fundamental investigation of the coked catalyst surface on a molecular level. Infrared (IR) spectroscopy is a technique which provides this type of information. The use of Fourier transform IR (FTIR) spectroscopy further allows examination of the catalyst surface under realistic reaction conditions. In the present study, FTIR spectroscopy was used to monitor changes on the catalyst surface during cracking reactions, including modification of surface hydroxyl groups, adsorption of hydrocarbons, and development of a highly carbonaceous coke species. In order to clarify the interpretation of the experimental results from this study, a brief discussion of what is known about the active sites in H zeolites for cracking reactions is required.

ACTIVE SITES IN H ZEOLITES

Zeolite cracking catalysts have been well characterized through numerous studies (*1–14*) using infrared spectroscopy, thermo-

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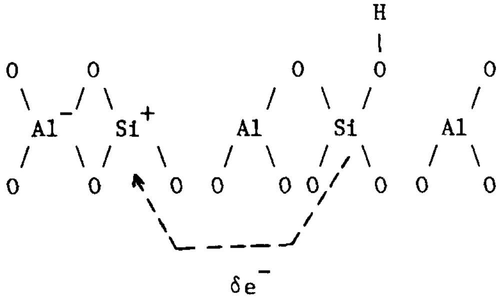
gravimetry, and other techniques. The acidic hydrogen forms have been found to be among the most active for catalytic cracking. Infrared investigations of hydrogen Y zeolite have revealed several peaks due to structural hydroxyl groups. A peak at 3640 cm^{-1} has been assigned to the acidic supercage hydroxyl groups thought to be important active sites in cracking reactions. Infrared studies of adsorption of bases (*3*) have shown these hydroxyl groups to be Brønsted acids. Heating the catalyst to temperatures above 400°C drives off structural water, and the extent of dehydroxylation that occurs affects the type and proportion of acidic sites present on the surface. As the supercage hydroxyl groups are driven off, electron-deficient Lewis acid sites are formed (*3*).

Catalytic cracking is an acid-catalyzed reaction, but the roles of the Brønsted and Lewis acid sites are not unequivocally defined. Early work (*11, 13*) suggested that Brønsted acid hydroxyl groups alone accounted for the catalytic activity of zeolites in a number of cracking reactions. Other investigations indicated, however, that Brønsted acid hydroxyl groups were not the only key to the high activity of zeolites in cracking. Liengme and Hall (*2*) found that dehydroxylated zeolites interacted with olefins even more strongly than zeolites with Brønsted hydroxyl groups. They asserted that carbonium ion formation in acid catalysis must proceed in other ways than just through Brønsted OH sites. Lunsford (*14*) and Hopkins (*15*) each noted that maximum catalytic activity for cracking reactions occurred with a catalyst calcined at a temperature higher than that required for maximum Brønsted acid site concentration; at the dehydration temperature for maximum activity, the Brønsted OH concentration had already passed its maximum and had declined considerably.

Lunsford (*14*), using the results of earlier workers (*16, 17*), proposed that catalytically active sites are formed by partial dehydroxylation of the zeolite to produce a small amount of what Uytterhoeven *et al.* (*1*) first termed "defect sites." These sites consist of SiO_3^+ and Al_4^- cation–anion pairs in the zeolite lattice. The zeolite also retains some Brønsted hydroxyl groups. Lunsford (*14*) postulated that the positively charged SiO_3^+ group acts inductively through the lattice on a Brønsted OH group to produce a partial negative charge across the lattice:



This electrostatic interaction between the Lewis acid site and the SiOH group reduces the hydroxyl group's electron density. This reduces the interaction between hydrogen and oxygen and makes the proton much more acidic. Although this theory still relies upon the presence of some Brønsted acid hydroxyl groups, it also suggests that Lewis acidity plays a role. This model appears to be more consistent with reaction data in which the maxima in reactivity and in Brønsted acidity do not correspond to the same calcination temperature of the catalyst (*14, 15*).

More recent work has suggested that the defect site mechanism of Uytterhoeven *et al.* (*1*) is a schematic representation of the formation of Lewis sites rather than a real one. The presence of trigonally coordinated aluminum was not found in dehydroxylated zeolites by Kuhl (*18*). Jacobs and Beyer (*19*) have found evidence to suggest that the true Lewis sites in zeolites are formed not from lattice groups but from Al–O species leached from the zeolite framework into the supercages during high-temperature treatment. Mirodatos and Barthomeuf (*20*) have found oxoaluminum deposits in the cavities of mordenite that are extremely strong acid sites. Therefore, while the true nature of the Lewis sites may differ from the representation shown above, the idea of synergism between Brønsted hydroxyl groups and Lewis sites is valid in any case.

Recent work by Langner and Meyer (*21*) supports the suggestion that both Brønsted and Lewis sites may be important in cracking reactions. They developed a mechanism for coke formation from butadiene on hydrogen Y zeolites in which Diels–Alder addition reactions proceed through Lewis acid sites, while Brønsted acid sites are required for hydride transfer reactions. Langner (*22*) has also postulated that adsorbed coke precursors participate in the cracking reactions, and that these precursors are cyclic in structure.

In their extensive work on the cracking of [2-^{13}C], methylpropene, Fajula and Gault (*23–25*) have also made the suggestion that more than one type of acidic site participates in cracking reactions. They proposed that strong sites are formed from interaction between Brønsted and Lewis acid sites, much like the theory of Lunsford.

Both Fajula and Gault (*23–25*) and Langner (*22*) have studied changes in product distributions with various changes in conditions during cracking reactions. Aromatic precursors to coke formation were suggested in both cases because of the presence of slight amounts of aromatic and cyclic compounds in the product stream.

The relationship between the active sites and the formation of coke on the catalyst during cracking reactions has been investigated. IR spectroscopy has been used previously to identify a highly carbonaceous surface species formed during cracking reactions (*26, 27*). The growth of a "coke" peak during reaction may be used to monitor coke formation as a function of reaction time, as well as to follow its relationship to the IR peak of the acidic hydroxyl groups. In the present study, the use of an *in situ* Fourier transform spectroscopic technique offers the advantage of extremely rapid data collection during the chemical reaction and a means of measuring overall coking.

EXPERIMENTAL

Materials. Y zeolite of the NH^{4+} form was purchased from Linde. High-purity (99%) 1-hexene (Aldridge) and 4-methylcyclohexene (J. T. Baker) were stored over a 4A molecular sieve prior to use. Helium gas of 99.99% purity was further purified before use by passage through an Oxy-clear unit.

Apparatus. A Nicolet 7199 Fourier transform infrared spectrometer was used to record the IR spectra. An *in situ* infrared cell was designed to be placed inside the spectrometer so that spectra could be recorded during reaction. The IR cell, a standard type of *in situ* cell (*11*), was encased by a resistance heater. KCl infrared windows were kept cool during high-temperature reaction by a copper water circulation system. Hydrocarbon reactants were supplied to the cell at 1 atm total pressure via a helium carrier stream from a gas bubbler system. The partial pressure of the hydrocarbon in the carrier stream was less than 20 Torr. The gas flow rate was approximately 60 cm^3/min.

Procedure. The NH_4Y zeolite was pressed into disks weighing approximately 45 mg and having a diameter of 2.54 cm. The sample was calcined in flowing oxygen and helium for 1 h at a temperature between 300 and 538°C, producing a partially or fully deammoniated and/or dehydroxylated HY catalyst, depending on the temperature used. The reaction temperature was 300°C for all experiments, and spectra were recorded every 3–5 min during the initial stage and frequently throughout the rest of the reaction.

RESULTS AND DISCUSSION

Pretreatment and Reaction Spectra

NH_4Y samples were calcined at temperatures between 300 and 538°C before reaction to remove ammonia and form the active HY catalyst. Figure 1 shows the

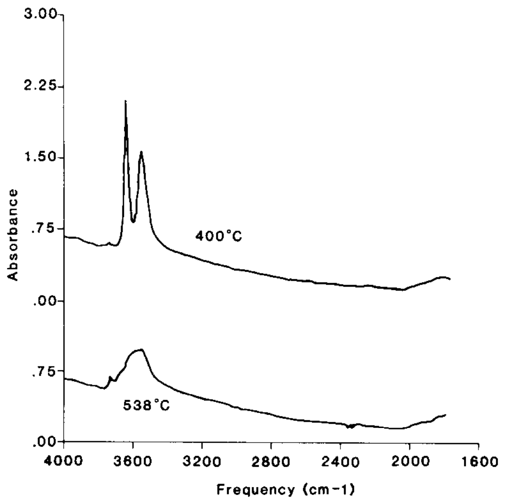


FIG. 1. FTIR spectra of HY catalysts calcined at 400 and 538°C.

spectra of two of the samples, calcined at 400 and 538°C. Below 400°C, the ammonia has only been partially removed, and spectral features of the NH_4^+ ions remain. As the temperature is raised, the ammonia is driven off, and the supercage OH peak at 3640 cm^{-1} grows to a maximum. Above 400°C, however, the dehydroxylation process replaces deammoniation, and the peak due to the Brønsted OH group in the zeolite supercage diminishes, until at 538°C it is merely a shoulder on the broadened 3540-cm^{-1} OH peak. This indicates that very little Brønsted acidity remains, while Lewis acid sites have been formed from the dehydration (*11*). The effect that this modification of the surface structure has on coke formation will be discussed.

FTIR spectra provide a sort of "time-lapse" picture of the catalyst surface during cracking reactions, as seen in Fig. 2A for the reaction of 1-hexene over an HY sample calcined at 400°C. The spectrum of the initial catalyst is shown along with those of the catalyst after 10 and 20 min of reaction. Several important modifications are to be noted. First, the Brønsted hydroxyl group at 3640 cm^{-1} is consumed during the reaction. Second, the formation of adsorbed hydrocarbons may be observed in the region 2800–3000 cm^{-1} and below 1500 cm^{-1}. And

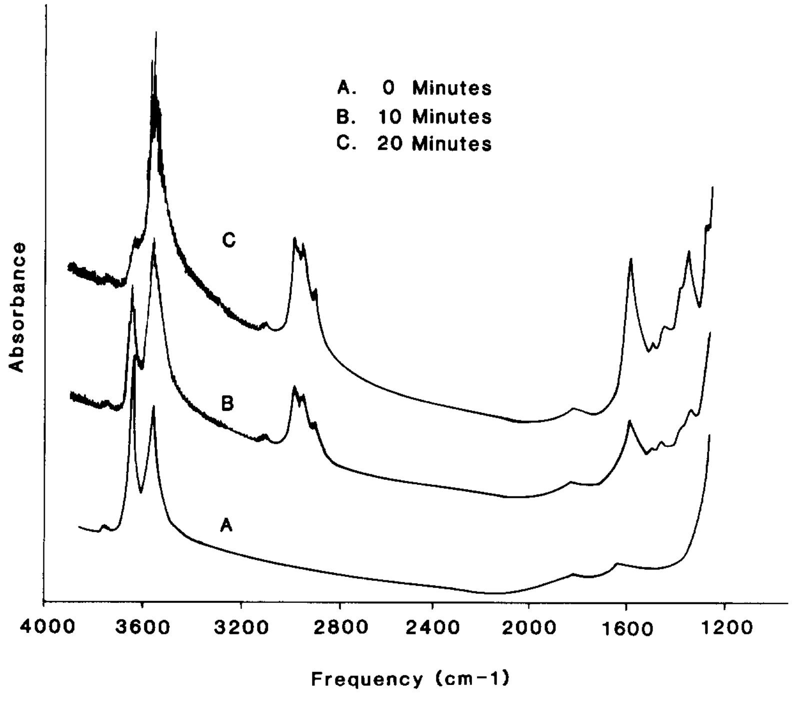


FIG. 2. FTIR spectra recorded during 1-hexene reaction at 300°C over HY catalyst calcined at 400°C.

third, a peak at about 1585 cm^{-1} is seen to grow during the reaction. This peak has been assigned to the highly carbonaceous coke species by previous authors (*26*, *27*).

Coke Formation

The carbonaceous species to which the peak at 1585 cm^{-1} is attributed has been studied previously using X-ray diffraction and light and electron microscopy (*28*). It is thought to consist partly of pseudographitic structures and partly of more disorganized material. The formation of these coke deposits as a function of reaction time may be plotted using the absorbance of the coke peak as a measure of coke concentration. This is shown in Fig. 3 for the 1-hexene reaction just discussed and also for the same reaction with a catalyst calcined at 538°C. The initial rapid increase in absorbance of the "coke" peak followed by a plateau is in agreement with results of current thermogravimetric coking studies being carried out in our laboratory.

FTIR spectroscopy offers a way to collectively monitor the formation of absorbing and/or scattering moieties as a function of time. In the collection of the interferogram the maximum signal is observed when the light paths in the two arms of the interferometer are equal (the zero displacement peak). At zero displacement all frequencies in the beam will interfere coherently; thus the intensity of the signal at zero displacement is a measure of the total power transmitted by the sample (independent of frequency) (*29*). The peak height of the zero displacement signal then measures the opacity of the sample averaged over the frequency range spanned by the source–detector combination (ca. 4500–425 cm^{-1} in our spectrometer). For a catalyst sample in which coke is forming, a diminution of this signal is as much a measure of scattering by "coke particles" as a measure of any frequency-specific absorption. The equivalent phenomenon in the transform spectrum is a general decrease in baseline transmission (increase in absorption) which is observed as the sample cokes. Figure 4 shows the decrease in the zero displacement peak as a function of time expressed as percentage transmission loss (ca. the region 4500–425 cm^{-1}) using the calcined catalyst as the 100% reference. The shape of the time curve is similar to that of the coke peak absorbance shown in Fig. 3, which indicates to us that the 1585-cm^{-1} peak corresponds to a vibration mode of the "coke" or at least to a moiety which forms at the same rate.

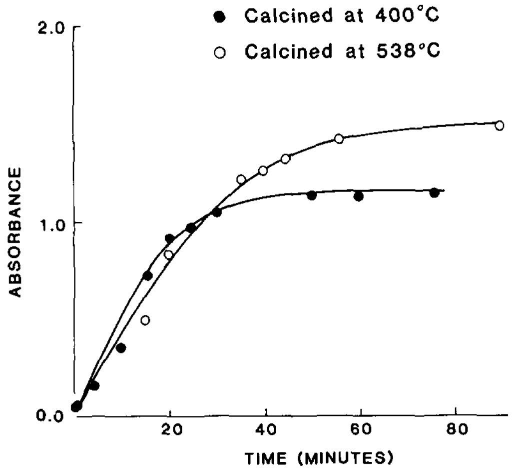


FIG. 3. Coke peak absorbance vs time for 1-hexene reactions at 300°C over HY catalysts.

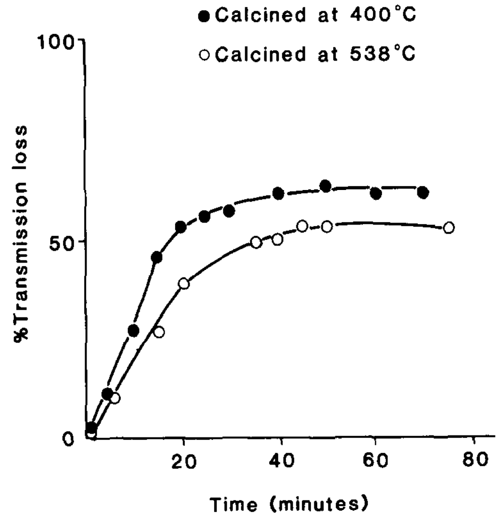


FIG. 4. FTIR transmission loss vs time for 1-hexene reactions at 300°C over HY catalysts.

These infrared spectroscopic results support the reaction study of Langner and Meyer (*21*) in which hydrocarbon adsorption and coke formation were found to be extremely rapid in the initial reaction stages, and then were diminished as the catalyst aged until no further hydrocarbon transformation occurred. Fajula and Gault (*24*) have also noted that most hydrocarbon residue is deposited in the early part of cracking reactions.

IR peaks in the region 1600–1300 cm^{-1}, including a peak in the same position as the coke peak, have been observed in IR spectra of the methanation reaction over Ru/Al_2O_3 (*30*). Peaks at 1585 and 1378 cm^{-1} were attributed to the OCO stretching vibrations of formate ions formed on the Al_2O_3 during methanation. Since a peak near 1585 cm^{-1} is observed during coking reactions, the possibility of formate formation from interaction of the hydrocarbon or its intermediates with the hydroxyl groups of the zeolite should be considered. Spectra of the 1-hexene reaction at lower temperatures also reveal a peak near 1380 cm^{-1} (*31*). However, the 1380-cm^{-1} peak undergoes a shift to lower frequency as temperature is increased, while the 1585-cm^{-1} peak remains in place. If these peaks are indeed due to the symmetric and asymmetric OCO vibrations of formate ions, they would be expected to change in tandem. They do not; this, together with the other information known about the 1585-cm^{-1} peak, supports the hypothesis that it represents a highly carbonaceous coke species.

Modification of Hydroxyl Groups

During the cracking reaction of 1-hexene described above, the growth of the coke peak was accompanied by a decrease in the concentration of Brønsted hydroxyl groups. This relationship is illustrated in Fig. 5. The striking linearity of the relationship lends support to the hypothesis that Brønsted acid hydroxyl groups do indeed act as active sites, at least for the formation of coke on cracking catalysts.

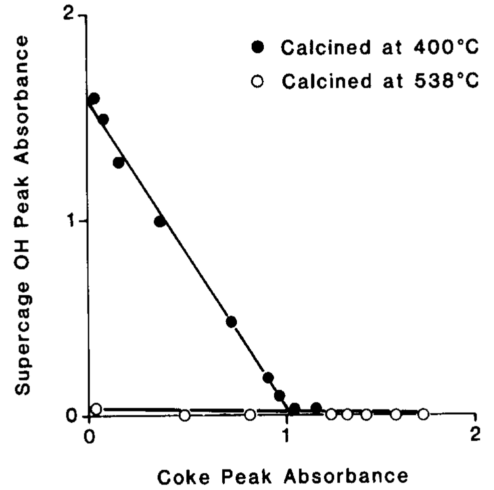


FIG. 5. Supercage hydroxyl absorbance vs coke peak absorbance for 1-hexene reactions at 300°C over HY catalysts.

This same linear curve was obtained for all reactions using catalysts calcined at 400°C or below, all of which exhibit large concentrations of Brønsted acid hydroxyl groups. For catalysts calcined at 538°C, however, such extensive dehydroxylation has taken place that the ordinate value for a plot of Brønsted OH absorbance vs coke peak absorbance would be approximately zero for any value of the abscissa. This is indeed the case, as is also shown in Fig. 5. The most interesting thing to note is that the amount of coke formed is significant for both catalysts, but the coke is formed on the dehydroxylated sample in the presence of only a very small amount of Brønsted acid sites. It appears that coking must proceed through sites other than just the Brønsted acid hydroxyl groups, or proceed by a parallel reaction.

The Nature of the Active Sites

The fact that two seemingly different catalyst sites are active for coke formation leads to the proposal of two different mechanisms for coke formation. Since the amount and composition of coke formed on each catalyst appeared to be not too dissimilar, the two types of sites probably are not radically different.

One possible explanation for the calcination temperature effect might be considered merely in terms of Brønsted and Lewis acidity: at lower calcination temperatures, the catalyst possesses Brønsted acid sites which are active for the formation of coke through a carbonium ion mechanism. As the calcination temperature increases, Brønsted acid sites are converted to Lewis acid sites, which are then the active sites for the reaction.

This explanation, while plausibly accounting for the results of the present study, contradicts the results of several other studies (*11, 13*) in which no relationship between Lewis acid sites and catalytic cracking activity could be found. In other work (*15*) the presence of Lewis sites was noted, and their synergistic effect on Brønsted sites was alluded to, but their role as active sites was not defined.

A compromise between the results of the present work and the findings cited above might be found in the proposed scheme of Lunsford (*14*) that was discussed earlier for partially dehydroxylated HY. The synergistic effect just noted could be accounted for by an inductive effect between a Brønsted Si–OH and a Lewis acid site farther down the lattice, as suggested in the defect site mechanism described earlier.

The electrostatic interaction creates a much stronger acid site at the OH group. In an extensively dehydroxylated sample such as that used in the present study, the number of these inductive sites would be small. Since they are much stronger than conventional Brønsted acids, a very few might be sufficient to produce the amount of coke observed in the reaction.

This dual-site mechanism for coke formation complements the results of other coking studies. Weeks *et al.* (*32, 33*) studied two similar catalysts and found similar product distributions and C:H ratios for reactions over hydroxylated and dehydroxylated samples. Since radiotracer experiments (*26*) have shown that zeolitic hydrogen is incorporated in coke deposits, it appears that the Brønsted hydroxyl group is involved in coking when it is present on the catalyst, but that coking and cracking reactions may proceed in its absence.

Langner (*22*) and Fajula and Gault (*23–25*) have also suggested that weaker Brønsted hydroxyl groups, as well as strongly acidic Lewis or Brønsted/Lewis sites, participate in cracking and coking reactions. Fajula and Gault supported this with their findings about changes in product distributions with calcination temperature of the H-mordenite catalysts.

Hydrocarbon Adsorption

All of the results discussed above were found to be valid for reactions with 4-methylcyclohexene, as well as with 1-hexene. The principal difference between these two hydrocarbons as reactants appeared to be that the initial coking rate was more rapid for 4-methylcyclohexene. The rise to the plateau in coke formation required only 15-20 min for 4-methylcyclohexene, compared with 25–30 min for 1-hexene. The tertiary carbon of 4-methylcyclohexene may form a carbonium ion with more ease than does 1-hexene.

The rapid coking found with 4-methylcyclohexene appears to support suggestions that ring compounds are preferential coke precursors, since coke deposits are thought to be aromatic in nature (*5, 21*). However, the C–H and ring mode absorption regions of the IR spectra showed little evidence of aromatic compounds adsorbed on the catalyst during reaction of either 4-methylcyclohexene or 1-hexene. Preliminary results for coking from toluene or methylcyclohexane have been found to be similar. The IR spectra from the reaction of 1-hexene (Fig. 2) show one small peak in the hydrocarbon adsorption region above 3000 cm^{-1}. Since this peak was still visible when the catalyst wafer was removed from the IR beam, we feel it is due to gas-phase 1-hexene. Some, but not all, of the stretching bands were also noted in the gas phase. This indicates lack of olefinic or aromatic adsorbed species. Any aromatic bands below 1200 cm^{-1} are obscured by vibrations of the zeolite structure. Methyl and methylene group peaks were observed, but these peaks changed very little as reaction progressed, except to intensify. Conversion of adsorbed hydrocarbon to aromatic coke precursors was not observed, and the growth of the coke peak at 1585 cm^{-1} was the only indication of the process of coke formation. One possible suggestion is that the reaction of hydrocarbon to form dehydrogenated coke species occurs so rapidly that the appearance of intermediates cannot be observed even by FTIR spectroscopy. The coke deposit which remains on the catalyst must then be so highly dehydrogenated that little or no aromatic –CH– linkages remain visible in the IR spectrum.

Since aliphatic $-CH_2-$ and CH_3- groups are observed to be adsorbed on the catalyst, another suggestion might be that the coke deposit consists of highly dehydrogenated linear or branched compounds which retain some aliphatic groups. This is supported by the spectra of Fig. 2 which show a peak at 1340 cm^{-1} which grows as coke is formed. This peak is assigned to tertiary C–H vibrations of branched hydrocarbons. These compounds could be formed by successive polymerization and hydrogen elimination reactions on the catalyst surface that proceed more easily than cyclization and aromatization reactions. The adsorption of 1-hexene and transformations of the adsorbed species during isothermal coking reactions are discussed in another paper (*31*).

Effect of Brønsted Acid Site Concentration

Since two types of active sites for coke formation on HY have been postulated in this investigation, depending upon the temperature of calcination of the sample, it would be interesting to note any differences in hydrocarbon adsorption between catalysts with Brønsted acidity and those that are highly dehydroxylated. Spectra for 1-hexene reaction over the two catalysts (Fig. 6) show that the hydrocarbon stretching region at 2800–3000 cm^{-1} and the deformation region below 1500 cm^{-1} are very similar, with one minor difference. The catalyst samples possessing a large concentration of Brønsted hydroxyl groups have a very small IR peak near 1500 cm^{-1} which is absent in the spectra of the dehydroxylated samples. This peak may be indicative of the presence of aromatic rings. Since the peak is a minor one, and with no further information about its molar absorptivity, quantitative conclusions cannot be drawn. However, the presence of this peak for some samples and not for the others may suggest differences in the structure of the coke species formed on each type of site. Coke formed from 1-hexene on a highly dehydroxylated sample may be less aromatic and more highly dehydrogenated in nature. Certainly neither catalyst exhibited signs of substantial amounts of adsorbed aromatic or polyaromatic species.

Conclusions

Coke formation over HY zeolites during cracking reactions of 1-hexene and of 4-methylcyclohexene has been investigated by *in situ* Fourier transform infrared spectroscopy. Catalysts containing Brønsted acid hydroxyl groups, as well as dehydroxylated catalysts, were used in an effort to determine the nature of the active sites for coke formation. It was found that coke formation was linearly proportional to the consumption of Brønsted acid hydroxyl groups. For dehydroxylated samples, however, coke formation proceeded in a manner similar to that of catalyst samples containing Brønsted acid hydroxyl groups. Brønsted acid sites appear to be a factor in coke formation, but certainly are not the only participants in the reaction.

A dual-site mechanism for coke formation was proposed following development of Lunsford (*14*) and of Uytterhoeven *et al.* (*1*). It is suggested that the active sites of the dehydroxylated sample are produced through an inductive effect of Lewis acid

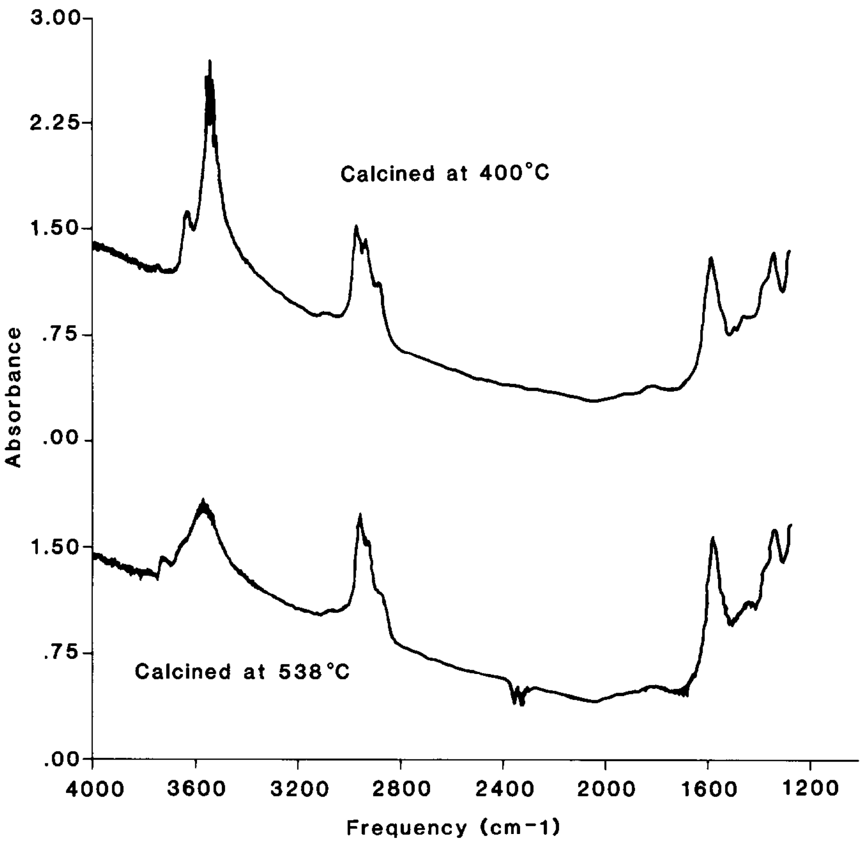


FIG. 6. FTIR spectra of 1-hexene reactions at 300°C over HY catalysts after 30 min of reaction.

sites on the few remaining supercage hydroxyl groups.

Hydrocarbon adsorption investigation showed little or no aromatic content of the material on the catalyst surface. The coke species appeared to be a highly dehydrogenated structure with some aliphatic residues. The composition of the coke formed from each type of active site appeared to be similar, with possibly a slighter higher aromatic content to the coke formed on the catalyst possessing Brønsted acid hydroxyl groups.

REFERENCES

1. Uytterhoeven, J. B., Christner, L. G., and Hall, W. K., *J. Phys. Chem.* **69**(6), 2117 (1965).
2. Liengme, B. V., and Hall, W. K., *Trans. Faraday Soc.* **62**, 3229 (1966).
3. Hughes, T. R., and White, H. M., *J. Phys. Chem.* **71**(7), 2192 (1967).
4. Angell, C. L., and Schaffer, P. C., *J. Phys. Chem.* **69**(10), 3463 (1965).
5. Eberly, P. E., Jr., *J. Phys. Chem.* **71**(6), 1717 (1967).
6. Bolton, A. P., and Lanewala, M. A., *J. Catal.* **18**, 154 (1970).
7. Gallei, E., and Eisenbach, D., *J. Catal.* **37**, 474 (1975).
8. Hildebrandt, R. A., and Skala, H., *J. Catal.* **12**, 61 (1968).
9. Ward, J. W., *J. Catal.* **13**, 321 (1969).
10. Ward, J. W., *J. Catal.* **11**, 259 (1968).
11. Ward, J. W., *J. Catal.* **9**, 225 (1967).
12. Ward, J. W., *in "Zeolite Chemistry and Catalysis"* (J. A. Rabo, Ed.), Chap. 3. ACS Monograph 171 Amer. Chem. Soc., Washington, D. C., 1976.
13. Benesi, H. A., *J. Catal.* **8**, 308 (1967).
14. Lunsford, J. H., *J. Phys. Chem.* **72**(12), 4163 (1968).
15. Hopkins, P. D., *J. Catal.* **12**, 325 (1968).
16. Richardson, J. T., *J. Catal.* **9**, 182 (1967).
17. Hirschler, A. E., *J. Catal.* **2**, 428 (1963).
18. Kuhl, G. H., *in* "Molecular Sieves" (J. B. Uytterhoeven, ED.), p. 227. Leuven Univ. Press, 1973.

19. Jacobs, P. A., and Beyer, H. K., *J. Phys. Chem.* **83**, 1174 (1979).

20. Mirodatos, C., and Barthomeuf, D., *J. Chem. Soc. Chem. Commun.* **1**, 39 (1981).

21. Langner, B. E., and Meyer, S., "Studies in Surface Science and Catalysis," Vol.6, "Catalytic Deactivation," p. 91, Elsevier, Amsterdam, 1980.

22. Langner, B. E., *J. Catal.* **65,** 416 (1980).

23. Fajula, F., and Gault, F. G., *J. Catal.* **68,** 291 (1981).

24. Fajula, F., and Gault, F. G., *J. Catal.* **68**, 312 (1981).

25. Fajula, F., and Gault, F. G., *J. Catal.* **68**, 329 (1968).

26. Eberly, P. E., Jr., Kimberlin, C. N., Jr., Miller, W. H., and Drushel, H. V., *Ind. Eng. Chem. Process Des. Dev.* **5**(2), 193 (1966).

27. Eisenbach, D., and Gallei, E., *J. Catal.* **56**, 377 (1979).

28. Haldeman, R. G., and Botty, M. C., *J. Phys. Chem.* **63**, 489 (1959).

29. A derivation of the fundamental equations of FTIR can be found in R. J. Bell, "Introductory Fourier Transform Spectroscopy" (Academic Press, New York, 1972), or in most books on physical optics.

30. Dalla Betta, R. A., and Shelef, M., *J. Catal.* **48**, 111 (1977).

31. Blackmond, D. G., Goodwin, J. G., Jr., and Lester, J. E., *J. Catal.* **78,** 247 (1982).

32. Weeks, T. J., Jr., Angell, C. L., Ladd, I. R., and Bolton, A. P., *J. Catal.* **33**, 256 (1974).

33. Weeks, T. J., Jr. and Bolton, A. P., *J. Chem. Soc. Faraday Trans.1* **70**, 1676 (1974).