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A Fourier-Transform Infrared Spectral Study of Propene Reactions on Acidic Zeolites

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The reactions of propene on the hydrogen forms of Y-zeolite, ZSM-5, and mordenite have been investigated using Fourier-transform infrared spectroscopy. After identical pretreatment conditions, propene reacts initially on all three zeolites to form an oligomer, identified by the growth of an IR band at ca. 1465 cm^{-1}, and also by characteristic perturbations of the surface hydroxyl stretching modes. At ambient temperature, oligomer formation occurs slowly on HY, at moderate speed on HZSM-5, and very quickly on HM. The oligomers formed on both HZSM-5 and HM are similar in CH_3/CH_2 ratio, and appear to be quite unbranched, whereas the oligomer formed on HY-zeolite is highly branched. At elevated temperatures, the oligomer transforms directly to coke on HY ($T > 200°C$), to aromatics on HZSM-5 ($T > 200°C$), and first to aromatics ($150°C \leq T < 250°C$) and then to coke ($T \gtrsim 300°C$) on HM. Little, if any, coke (identified by a characteristic band near 1600 cm^{-1}) is formed on HZSM-5, Blocking the strong Brønsted sites on HY-zeolite and HM did not prevent oligomer formation, but subsequent coke formation did not occur.

INTRODUCTION

In a previous study, it was found that the activity of hydrogen mordenite (HM) for cumene cracking decreased rapidly with time on stream (*1a*). Under identical conditions, hydrogen Y-zeolite also deactivated quickly, while hydrogen ZSM-5 (HZSM-5) was found not to deactivate at all (*1b*). It is well known that carbonaceous material (coke) is formed during such reactions, and the differences in the rate of deactivation presumably reflect differences in the rate of coke formation over these three zeolites.

Coke formation is a complex reaction, and the factors which affect the mechanism of its production are not well understood. The situation regarding coke formation from 1-hexene over Y-zeolite illustrates the difficulties involved: Blackmond *et al.* (*2*) observed no aromatic compounds prior to coke formation, while Wojciechowski and co-workers (*3, 4*) report that at 260°C, cyclization of 1-hexene to aromatic ring structures has occurred. While the method used to detect coke formation may account for some of the differences (Blackmond *et al.* used *in situ* IR spectroscopy, while Wojciechowski and coworkers used high temperature desorption prior to elemental analysis to identify the coke) it is also clear that for comparative studies on different catalysts, identical conditions are essential.

In cumene cracking, polymerization of the propene formed in the initial step of the reaction is thought to be responsible for at least part of the coke (*5, 6*). It is the purpose of this work to use infrared spectroscopy to study the adsorption and reaction of propene over the three catalysts HM, HY, and HZSM-5, to obtain more information about the deactivation of these catalysts during cumene conversion. Propene reactions over Y-zeolite have been studied quite extensively (*7–9*) and some studies of propene on ZSM-5 have been reported (*10–12*), although they do not include any detailed infrared work. Haber *et al.* (*9*) have carried out some work with HZ-79, a catalyst similar to ZSM-5, but no reports of the

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reactions of propene over H-mordenite have appeared. Mordenite is an important industrial catalyst, with channel dimensions very similar to those of ZSM-5, yet it is known to be much more subject to coke-induced deactivation. In the work reported here, an IR cell which holds as many as four catalyst samples at one time was used, so that pretreatment and reaction conditions would be identical. It was hoped that in this way any differences in the mechanism of the formation of coke from propene over these three catalysts would be revealed.

EXPERIMENTAL

Materials. The ammonium forms of zeolites Y and mordenite (obtained from Union Carbide) and ZSM-5 (Mobil) were used directly. These transformed into their H form during activation at 500°C under evacuation and they will be denoted as HY, HM, and HZSM-5, respectively.

Propene (Matheson) was 99.0% pure and was used without further treatment. 2,6-Dimethylpyridine (DMPy) used to poison Brønsted sites selectively was obtained from K & K Laboratories (California) and was dried over molecular sieves and degassed by several freeze–pump–thaw cycles before use.

Pretreatment of zeolite. For the infrared studies, self-supporting wafers (13 mm diameter) were made from ca. 20 mg of zeolite. The IR cell can hold wafers of HY, HZSM-5, and HM simultaneously so that different samples can be subjected to identical treatment before their spectra are recorded. A standard pretreatment for the samples was used: The cell containing the zeolite wafers was evacuated while slowly increasing the temperature to 500°C at which time oxygen was admitted and left overnight at the same temperature to remove any carbonaceous contaminants. The sample was finally evacuated at 500°C for 2 h and then cooled to room temperature to record zeolite background spectra.

Infrared measurements. Infrared spectra were measured at 2 cm^{-1} resolution on a Nicolet 8000 Fourier transform spectrometer. Because the initial reactions of propene can occur very quickly over these acidic catalysts at elevated temperatures, the spectra were first measured as a function of time at room temperature. After the background spectra of the three pretreated zeolites were recorded, a small dose of propene (ca. 70 μmol) was allowed to enter the cell, and spectra were recorded over a 4-h period. In a second experiment, using new zeolite pellets, the reactions which occur at elevated temperature were monitored. After addition of propene, the cell was held at 50°C for 15 min, and then IR spectra were measured (after cooling to room temperature). The furnace temperature was then increased in 50°C steps to 400°C, recording spectra after 15 min at each temperature. In a third experiment, designed to identify the sites responsible for coke formation, DMPy was adsorbed onto the surfaces, then partially desorbed (at 300°C) before propene addition.

RESULTS AND DISCUSSION

Zeolite Hydroxyls

The infrared spectra of the three pretreated catalyst samples (zeolite Y, H-mordenite, and HZSM-5) prior to propene adsorption are shown in Figs. 1a, 2a, and 3a. The hydroxyls which give rise to the 3745 cm^{-1} band, which is common to all these catalysts, are weakly acidic and have been attributed to amorphous SiO_2 inside and/or outside the zeolite crystallites; this band may also contain some contribution from Si–OH groups in regions of the zeolite which are low in aluminum (*13–15*). Zeolite Y has two other OH stretching vibrations; the stronger band, at 3650 cm^{-1}, arises from highly acidic hydroxyls which are situated in the large cavities, and are responsible for most of the Brønsted acidity of this catalyst, while the OH groups associated with the 3550 cm^{-1} band are located in the β

TABLE 1

The IR Spectrum of Propene above 1300 cm^{-1}[a]

Gas	In Ar matrix	Assignment
3090	3091 (s)	CH$_2$ asym. str.
—	3036 (s)	CH str.
2992	2983 (s)	CH$_2$ sym. str.
2954	2941 (s)	CH$_3$ asym. str.
2933	2923 (s)	CH$_3$ asym. str.
2870	2859 (m)	CH$_3$ sym. str.
1652	1650 (s)	C=C str.
1474	1453 (vs)	CH$_3$ asym. def.
1443	1439 (s)	CH$_3$ asym. def.
1419	1415 (m)	CH bend
1378	1373 (w)	CH$_3$ sym. def.

[a] From Ref. (*17*).

cages of the structure and are less accessible (*16*). Both HM and HZSM-5 have only one other OH stretching vibration, at ca. 3610 cm^{-1}, in addition to the 3745 cm^{-1} band. The hydroxyls responsible for this 3610 cm^{-1} mode are very acidic.

Propene Adsorption

(*a*) *At ambient temperature.* The assignment of the infrared spectrum of propene adsorbed on these zeolites is facilitated by comparison with its spectrum in the vapor phase and as a solute in an inert gas matrix at low temperature (*17*); these assignments are given in Table 1. As seen in Fig. 1 the spectrum of propene adsorbed on HY shows bands at about 2960 and 2930 cm^{-1} assigned to asymmetric CH$_3$– and –CH$_2$– stretching vibrations respectively, and a band at 2874 cm^{-1} attributed to symmetric C–H vibrations. A band arising from the C=C stretching vibration is seen at 1633 cm^{-1}, and the bands of the CH$_3$– and –CH$_2$– deformation modes are observed at ca. 1465 and 1380 cm^{-1}. Upon adsorption of propene, the IR bands of the acidic hydroxyls of the zeolites shift to lower wavenumber. In the case of zeolite Y, as has been reported previously (*7, 8*), the OH band at 3650 cm^{-1} is slowly shifted to ca. 3200 cm^{-1} (over about 1 h) by hydrogen bonding to propene. After several hours both the 3200 cm^{-1} band and the C=C band at 1633 cm^{-1} disappear, the former being replaced by a broad band at ca. 3535 cm^{-1}, which overlaps the band at 3550 cm^{-1} attributed to the hydroxyls in β cages (see above). This change has been interpreted as resulting from the slow polymerization of the adsorbed propene effected by the zeolite even at room temperature (*7*). It seems certain the the broad 3535 cm^{-1} band arises from the acidic hydroxyls of the zeolite surface interacting with a saturated hydrocarbon, i.e., an oligomer of propene. Hexane adsorbed on zeolites X and Y produces a band close to this location (*7*), but alkene and

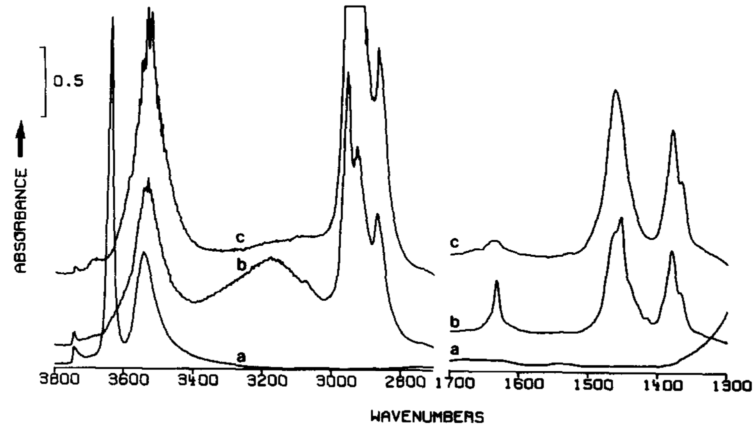


FIG. 1. Infrared spectra of HY zeolites: (a) Before propene adsorption. (b, c) At different times after propene adsorption and reaction at ambient temperature: (b) 2 h 30 min, (c) 22 h.

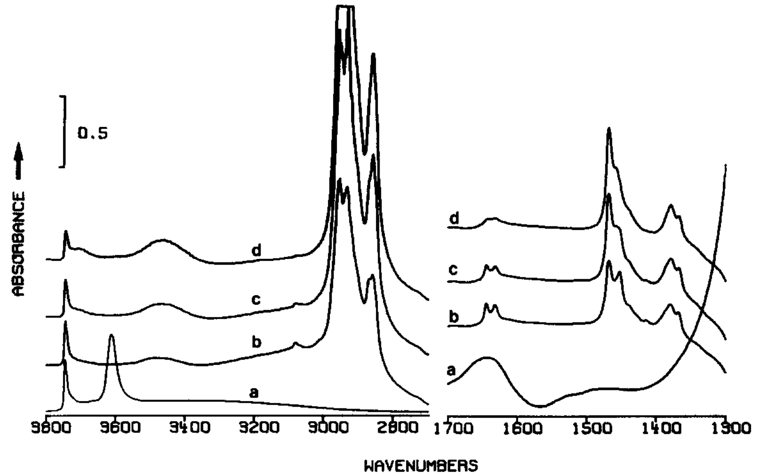


FIG. 2. Infrared spectra of HZSM-5 zeolite: (a) Before propene adsorption. (b–d) At different times after propene adsorption and reaction at ambient temperature: (b) 1.5 min, (c) 37 min, (d) 4 h 13 min.

aromatic compounds produce shifts of the O–H stretch to much lower wavenumber (ca. 3300 cm^{-1} for benzene and toluene (*18*), and 3200 cm^{-1} for propene as seen above).

The behavior of HZSM-5 upon propene adsorption is somewhat different as shown in Fig. 2. Even at room temperature, propene interacts very quickly with the acidic hydrogens (3610 cm^{-1}) of HZSM-5 as shown by the immediate disappearance of this band as its shifts to lower wavenumber. The less acidic hydroxyls (3745 cm^{-1}) also interact with the propene but much more slowly, as shown by the very slow decrease in the intensity of the 3745 cm^{-1} band. Two distinct C=C stretching vibrations of adsorbed propene can be seen at 1646 and 1632 cm^{-1} which disappear with time. These bands probably represent propene adsorbed on the two distinct OH groups (3745 and 3610 cm^{-1}). This assignment is based on the observation that their disappearance with time is accompanied by an increase in intensity of bands at 3460 (broad) and ca. 3710 cm^{-1}, which are associated with oligomer formation. The 3460 and 3710 cm^{-1} bands arise from the OH groups of the zeolite (at 3610 and 3745 cm^{-1}, respectively) interacting with this oligomer. A band at 1469 cm^{-1} also increases in intensity with time. This band represents the $-CH_2-$ deformation of the oligomer itself (*8*).

The reaction of propene with mordenite also occurs very quickly even at room temperature as can be seen in Fig. 3. The strong acid sites (3608 cm^{-1}) disappear immediately. No clear C=C stretch of adsorbed propene can be seen, and oligomer formation, as evidenced by the appearance of $-CH_2-$ band at 1468 cm^{-1}, is almost complete after only 8 min. Very little change takes place in the next 4 h, except for a slight increase in the intensity of the bands already present. There is a band at ca. 3695 cm^{-1} which must represent the less acidic OH (3745 cm^{-1}) interacting with the oligomer; these 3745 cm^{-1} hydroxyls must be more acidic in HM than in the other two zeolites, as evidenced by the more rapid disappearance of the 3745 cm^{-1} band. The unusual feature is the presence of two broad bands below 3600 cm^{-1} (at 3586 and 3516 cm^{-1}). In HZSM-5 and Y zeolite only one band (attributed to strong acid sites interacting with oligomer) appeared in this region. There is also a weak band at 1537 cm^{-1} which may indicate the formation of aromatics, even at room temperature. No

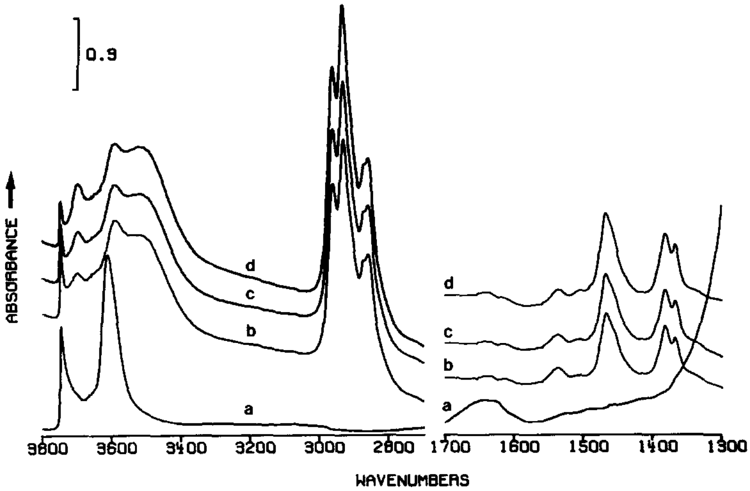


FIG. 3. Infrared spectra of H-mordenite: (a) Before propene adsorption. (b–d) At different times after propene adsorption and reaction at ambient temperature: (b) 8.5 min, (c) 45 min, (d) 4 h 30 min.

evidence for any coke formation is seen at this low temperature on any of the catalysts (see discussion below).

Structure of the oligomer. The relative integrated intensities of the overlapping bands at ca. 2960 and ca. 2930 cm^{-1} assigned respectively to the CH_3– and –CH_2– asymmetric stretching vibrations of the oligomer were calculated using a curve analysis program. The intensity ratios were found to be reasonably consistent for different experiments, being 0.40 ± 0.06 for HZSM-5, 0.44 ± 0.08 for HM, and 1.58 ± 0.07 for HY. These ratios do not change with time once the oligomer forms. The much greater relative strength of the CH_3–associated bands for the oligomer formed on zeolite Y indicates that it is considerably more branched than those formed on either HZSM-5 or HM. If it is arbitrarily assumed that the oligomers formed in the two latter cases are essentially linear, it is possible to calculate their chain length, using the procedure outlined by Jones (*19*) (also see Eisenbach and Gallei (*20*)). According to Jones, the intensity of the 2960 cm^{-1} (CH_3) band is $8.0n + 258$, and that of the 2930 (CH_2) band is $77n - 18$, where n is the number of methylene groups in the chain. Using a relative intensity ratio $I_{2960}/I_{2930} = 0.42$ for HZSM-5 and HM, n is found to be ca. 10, which would imply that the saturated oligomer is formed from four propene molecules. It must be recognized, of course, that the accuracy of this calculation depends very much on (a) the arbitrary assumption that the oligomers formed on HY and HZSM-5 are linear, and (b) the assumption that the intensities derived by Jones for solutions can be applied to adsorbed molecules. However, even if the above calculation is not accurate, the conclusion that the oligomer formed from propene on HY is much more branched than that formed on either of the other two catalysts is unquestionable.

(*b*) *At elevated temperatures*. As the temperature is raised, starting with fresh HY and propene, the reaction of propene to form oligomer occurs more quickly; as shown in Fig. 4, the intensity of the oligomer bands at 1464 cm^{-1} and at ca. 3535 cm^{-1}increases. However, at about 200°C the oligomer band at 1464 cm^{-1} starts to decrease in intensity, as does the broad band at 3535 cm^{-1} (although this is harder to see, because of the underlying 3545 cm^{-1} OH band). In addition, bands near 1590 and 1341 cm^{-1} start to grow. The 1590 cm^{-1} band has been attributed to the C=C

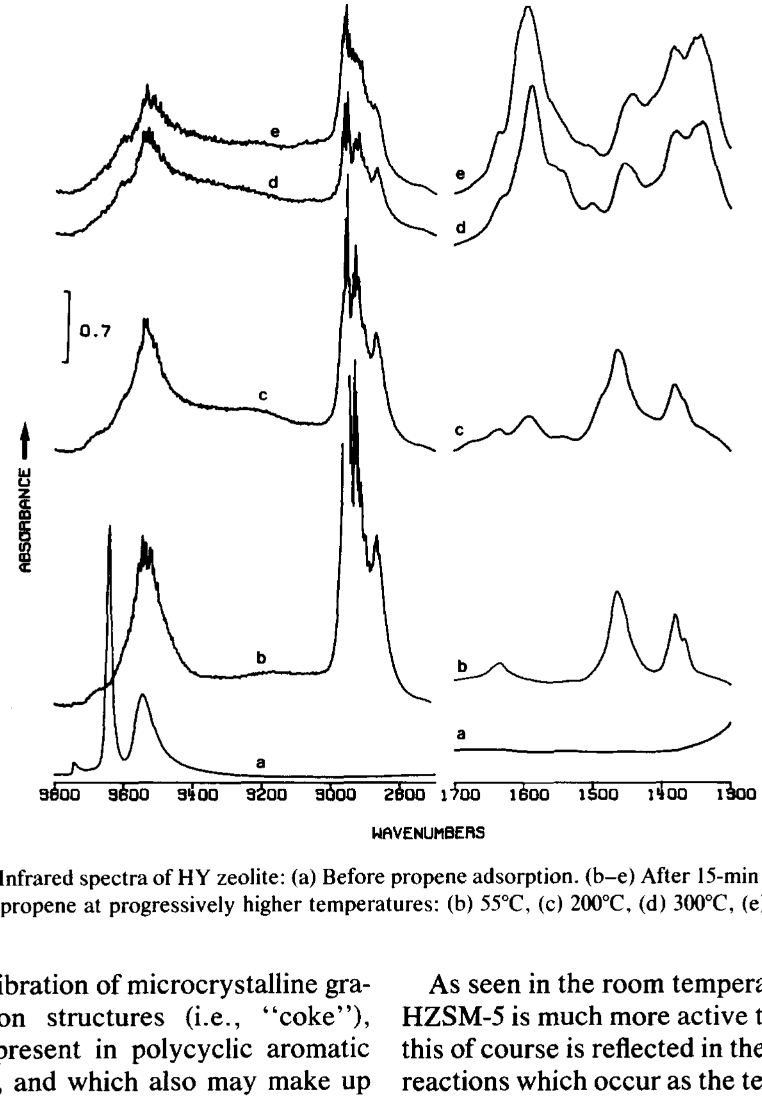


FIG. 4. Infrared spectra of HY zeolite: (a) Before propene adsorption. (b–e) After 15-min reaction of adsorbed propene at progressively higher temperatures: (b) 55°C, (c) 200°C, (d) 300°C, (e) 400°C.

stretching vibration of microcrystalline graphitic carbon structures (i.e., "coke"), which are present in polycyclic aromatic compounds, and which also may make up the carbonaceous deposits on catalysts (*21*). The broad absorption at ca. 1341 cm^{-1} probably also is associated with coke. In addition to the 1590 cm^{-1} band, a broad intense absorpion at ca. 1360 cm^{-1} has been observed in ground graphites, carbon blacks, and activated carbons (*22*). The position of this latter band was found to be sensitive to particle size (*22*), and it is not unreasonable that in the zeolitic environment it could appear at ca. 1341 cm^{-1}. By 350°C the 1464 cm^{-1} oligomer band is almost completely gone, and the coke bands are very strong. No new bands in the OH stretching region can be seen.

As seen in the room temperature studies, HZSM-5 is much more active than HY, and this of course is reflected in the speed of the reactions which occur as the temperature of a sample of propene adsorbed on HZSM-5 is raised. After 15 min at 50°C the spectrum is very similar to that obtained after 4 h at room temperature, except that oligomer interaction with the 3745 cm^{-1} hydroxyls has proceeded even more quickly (see Fig. 5). Little further change is noted, except in the increasing intensity of these bands, until 200°C, when a new band at 1510 cm^{-1} starts to appear. By 250°C, it is clear that the 1469, 3460, and 3710 cm^{-1} oligomer bands are getting weaker, and a new broad band at 3585 cm^{-1} appears. The 1510 cm^{-1} band gets stronger, and a weak band at ca. 1610 cm^{-1} begins to appear. Also, a fairly sharp,

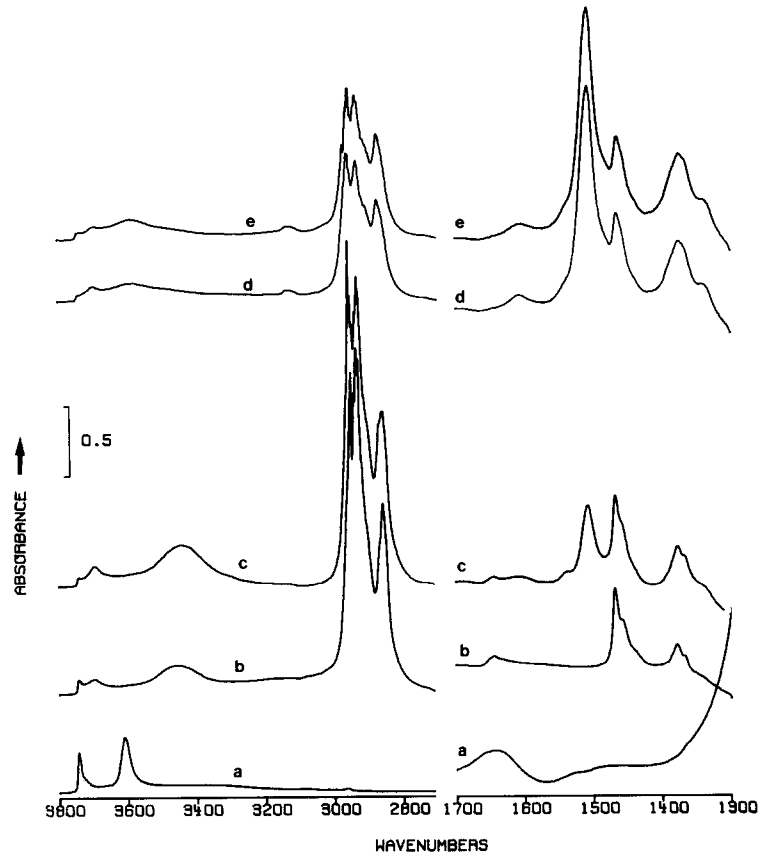


FIG. 5. Infrared spectra of ZSM-5: (a) Before propene adsorption. (b–e) After 15-min reaction of adsorbed propene at progressively higher temperatures: (b) 55°C, (c) 200°C, (d) 300°C, (e) 400°C.

weak band at 3130 cm^{-1} starts to grow. All of these observations are consistent with the conversion of the oligomer into other products. The 1510 cm^{-1} band represents an aromatic C=C stretch (*9, 11*); it is notable that only one fairly sharp band is seen in this region, suggesting that the aromatics formed are similar to each other; a wide range of aromatics would give more bands. The products desorbed from the HZSM-5 surface after this reaction with propene at 300°C were analyzed using GC–MS. The results were very similar to those obtained by Vedrine *et al.* (*23*) from a GC study which show that toluene, ethylbenzene, and xylenes represent more than 80% of the aromatic products when propene reacts over ZSM-5. As the band at 3130 cm^{-1} is higher than expected for an aromatic C–H stretch, it may represent the surface OH groups hydrogen bonded to these aromatics. The OH groups on NaHY zeolite (77% H) shift 326 and 350 cm^{-1} after adsorption of benzene and toluene, respectively (*18*). As the magnitude of the H-bonding shift is a measure of the strength of the interaction (*7*), a shift from 3610 to 3130 cm^{-1} is reasonable for the much more acidic hydroxyl groups of HZSM-5, in the presence of simple aromatics. Whether the 3585 cm^{-1} band represents the 3745 cm^{-1} hydroxyls H-bonded to aromatics or the 3610 cm^{-1} hydroxyls perturbed by interactions with saturated alkanes is not clear.

The observation of the formation of aromatics from propene on HZSM-5 at $T \geq$ 200°C requires some comments, in view of the recent report by Abbot *et al.* (*3*) that

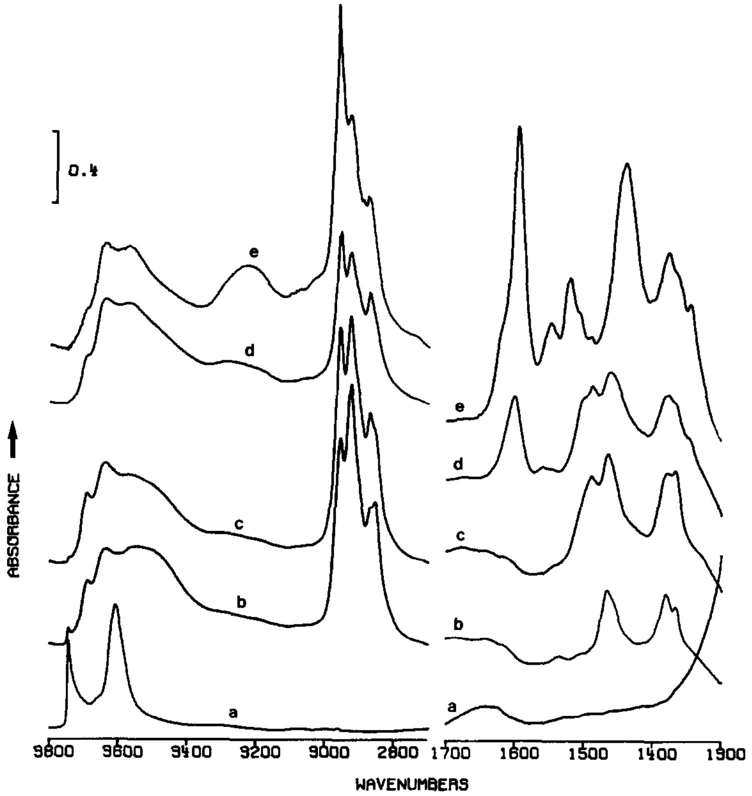


FIG. 6. Infrared spectra of H-mordenite: (a) Before propene adsorption. (b–e) After 15-min reaction of adsorbed propene at progressively higher temperatures: (b) 55°C, (c) 200°C, (d) 300°C, (e) 400°C.

after reaction of 1-hexene over HZSM-5 at temperatures up to 280°C polyenes and cyclic structures were not detected; the residual material remaining on the catalyst after reaction at these temperatures was found to be mainly adsorbed olefins. Part of this difference may of course result from the use of propene as reactant in this work, rather than 1-hexene. However, some of the difference may be attributed to the method of analysis. *In situ* FTIR spectroscopy can identify species present on the surface, while the elemental analysis of the residual material carried out by Abbot *et al.* (*3*) involved a high temperature (500°C) stripping of the residue from the catalyst surface, during which thermal cracking could affect the structure of the compounds desorbed. The observation of aromatic formation from propene over HZSM-5 is consistent with earlier reactivity studies (*24, 25*).

As the temperature of a fresh sample of H-mordenite with adsorbed propene is raised to 150°C a band at 1490 cm^{-1} starts to appear (see Fig. 6). This band increases in intensity until ca. 250°C, but at 300°C and above it diminishes, being replaced by another at 1523 cm^{-1}. The band at 1490 cm^{-1} must be analogous to the 1510 cm^{-1} band seen on HZSM-5 (see above); i.e., it must arise from adsorbed simple aromatics. (On Y zeolite, for example, benzene absorbs at 1477 cm^{-1} and toluene at 1495 cm^{-1} (*18*).) The bands between 1500 and 1525 cm^{-1} which appear at higher temperature presumably arise as the simple aromatics are converted to a mixture of more complex aromatics, perhaps *para*-substituted ones, which absorb in this region (*26*). At 250°C a weak band at ca. 1596 cm^{-1} starts to appear; this must be attributed to the onset of coke formation (see above). As the temperature is raised, this band rapidly becomes stronger, and at the same time the overall intensity of the bands of the aromatic compounds (1490–1525 cm^{-1}) decreases. Apparently in the case of mordenite, coke is formed via aromatic precursors, not directly from the oligomer as is the case for zeolite Y. As these aromatic compounds and coke are being formed, the 1465 cm^{-1} "oligomer $-CH_2-$ band" is replaced by a lower wavenumber band (1442 cm^{-1} at 400°C) which may arise from aliphatic groups attached to the aromatic rings; unsaturation next to a CH_2 group lowers the frequency to its deformation vibration to about 1440 cm^{-1} (*26*).

The behavior of the 3745 cm^{-1} OH stretching vibration at elevated temperatures is different in HZSM-5 and H-mordenite. In the case of HZSM-5 it becomes weaker as the OH groups hydrogen bond to the propene, but in H-mordenite, under identical conditions, it disappears completely. Clearly the hydroxyl groups responsible for this vibration are more active in mordenite than in ZSM-5, either because they are more accessible or because they are intrinsically more acidic. It would appear that these hydroxyls may be responsible for the weak Brønsted activity identified by Fajula and Gault by gas chromatography (*27*), while the stronger Brønsted activity they observe is of course associated with the hydroxyls which absorb at 3610 cm^{-1}.

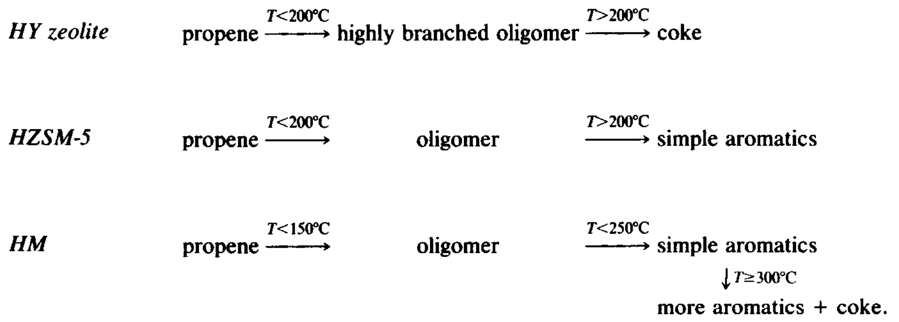
Active Sites for Coke Formation

It is well known that pretreatment at temperatures above 400°C causes dehydroxylation of zeolites, resulting in a decrease in the number of Brønsted sites and an increase in the number of Lewis sites. This is reflected in the IR spectra, where the intensity of the acidic OH stretching bands decreases with increasing pretreatment temperature. Although the IR spectra of adsorbed pyridine show that all three zeolites studied here possess Lewis sites (with HZSM-5 containing far fewer than either HM or HY) they cannot by themselves be the active sites for coke formation. When propene is adsorbed and then heated on samples pretreated at different temperatures, those pretreated at higher temperature, viz., ≥650°C, show much less coke (as evidenced by the 1600 cm^{-1} IR band) than those pretreated at lower temperatures.

However, the involvement of Brønsted sites in coke formation appears clear. There is a direct correlation between the concentration of Brønsted sites and the intensity of the coke band at ca. 1600 cm^{-1} in HY and HM catalysts (2). Further understanding of the role the Brønsted sites play in coke formation was found by adding DMPy to the cell containing the zeolites, then evacuating at 300°C for 30 min. DMPy adsorbs strongly on Brønsted acid sites and only weakly on Lewis acid sites (*28*). After high temperature desorption, DMPy is completely removed from the Lewis sites, and also desorbed from the weaker Brønsted sites. However, in the case of HY and HM, as shown by the IR spectra, the strong Brønsted sites are still blocked. (For H-ZSM-5, poisoning by DMPy was negligible, and therefore this experiment was not informative for this catalyst.) For mordenite and zeolite Y, subsequent addition of propene followed by heating for 15 min at 300°C caused propene oligomerization to occur, as shown by the infrared spectra, but the transformation of the oligomer into aromatics (expected on HM) or coke (expected on both HM and HY) did not occur. In the absence of DMPy, similar procedures would have produced strong coke bands on HM and HY. It appears that the weaker Brønsted sites (not blocked by DMPy) are capable of catalyzing propene oligomerization but that coke formation requires the availability of the stronger Brønsted sites which were still blocked by DMPy in this experiment.

CONCLUSION

Even under identical pretreatment and reaction conditions the reactions of propene adsorbed on the three catalysts HY-zeolite, H-mordenite, and HZSM-5 are quite different:



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\begin{array}{lll}
\textit{HY zeolite} & \text{propene} \xrightarrow{T<200^\circ\text{C}} \text{highly branched oligomer} \xrightarrow{T>200^\circ\text{C}} \text{coke} \\
\textit{HZSM-5} & \text{propene} \xrightarrow{T<200^\circ\text{C}} \text{oligomer} \xrightarrow{T>200^\circ\text{C}} \text{simple aromatics} \\
\textit{HM} & \text{propene} \xrightarrow{T<150^\circ\text{C}} \text{oligomer} \xrightarrow{T<250^\circ\text{C}} \text{simple aromatics} \xrightarrow{T\geq 300^\circ\text{C}} \text{more aromatics + coke.}
\end{array}
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It is clear that coke can form either directly from a highly branched, nonaromatic oligomer (on HY) or, as on H-mordenite, via a two-step process which involves the transformation of a relatively unbranched oligomer into aromatic compounds prior to coke formation. On HZSM-5 the formation of oligomer and, subsequently, aromatic compounds is evident, but even at 400°C no coke formation occurs.

Hydrogen mordenite is clearly the most reactive catalyst of these three for propene conversion to hydrocarbon products while hydrogen Y-zeolite is the least reactive. It is interesting to note that coke readily forms on these two catalysts, but not on HZSM-5, which is intermediate for propene reactivity.

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