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Infrared Diffuse Reflectance Study of the Silicon-Rich H–ZSM-5 Catalysis of Ethanol Conversion

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A new infrared diffuse reflectance reactor was used to study the *in situ* H–ZSM-5 catalyzed conversion of ethanol to high-purity ethylene between ambient temperature and 400°C. Zeolites having a Si/Al atom ratio of 35 to 126 adsorbed ethanol principally on aluminol acid sites, while silicon-rich materials of Si/Al greater than 500 adsorbed ethanol on both terminal silanol sites and intracrystalline hydrogen-bonded silanols. The silicon-rich materials demonstrated hydrogen-bonded silanol functionalities in their intracrystalline structures which became prominent as the silicon content increased. A portion of these silanols was removed from the infrared spectrum upon treatment with dilute sodium hydroxide demonstrating their acidity. The *in situ* infrared data showed that ethanol conversion to ethylene using zeolites of low Si/Al ratio utilized aluminum-based Brønsted acid sites while the activity of the silicon-rich materials was based on the hydrogen-bonded silanols. © 1989 Academic Press, Inc.

INTRODUCTION

The catalysis of the conversion of aqueous ethanol to high-purity ethylene by silicon-rich H–ZSM-5 materials (*1*) demonstrated unusually high activity and selectivity as the Si/Al atom ratios increased. The studies suggested that an especially reactive silanol functionality appeared in these zeolites as the silicon content increased which was responsible for maintaining the ethanol conversion activity at unexpected high levels. The purpose of this study was to understand this catalysis by spectroscopically comparing H–ZSM-5 materials of different silicon contents using a new Fourier-transform infrared diffuse reflectance reactor (*2*). In addition to the scientific issues related to zeolite catalysis which this *in situ* spectroscopic study examines, the capabilities of the new diffuse reflectance cell are described here in detail as an alternative to the transmission type of analyses which have been commonly utilized for such studies in the past.

The advantages of the diffuse reflectance method described here are principally the following: (i) Powdered samples which are similar to the form used in typical laboratory catalysis studies may be used. (ii) It avoids the sample preparation technique commonly used in transmission methods where the sample is pressed into a thin wafer at high pressures. This may lead to pore closure and diffusion limitations when the subject catalytic reaction is fast. (iii) It facilitates the analysis of poorly transmitting and opaque materials. (iv) Since it is a reflectance technique with an inherently short path length through the sample, it permits IR analyses in strongly absorbing regions of the spectrum where transmission methods often cut off. (v) It permits a more accurate measurement and control of the temperature of the catalyst. (vi) It uses a configuration for passing a reacting gas through the catalyst bed which is similar to typical catalysis studies and the cell permits the utilization of gases at high pressures.

The infrared spectrum of H–ZSM-5 was examined by Vedrine and co-workers (*3*) previously as a function of the effect on their spectrum by dealumination and high-temperature calcination. The changes in the

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infrared spectrum in the hydroxyl region as a function of the Si/Al atom ratio demonstrated (*4, 5*) that a hydrogen-bonded silanol appeared as the silicon content of the zeolite increased. The recently reported studies by Woolery and co-workers (*4*) examined these spectra up to a Si/Al atom ratio of 13,000. Temperature-dependent studies (*5*) on a material having a Si/Al atom ratio of 1062 showed that upon dehydration of the sample at 400°C both terminal and hydrogen-bonded silanols appeared in the infrared and that the hydrogen-bonded species intensified and moved to lower absorption frequencies as the temperature was decreased. Both ammonia and pyridine adsorption (*6*) were utilized by infrared analysis to characterize the distribution of Brønsted and Lewis acid sites in these materials.

This report examines the *in situ* infrared spectra of H–ZSM-5 zeolites having Si/Al atom ratios of 35 to 5000 while they catalyze the conversion of ethanol to ethylene using a new diffuse reflectance flow reactor. The study first characterized the materials by infrared spectroscopy as a function of their silicon content. Then, the reaction of ethanol with the silanols and aluminols in samples of varying atom ratio was studied as a function of reaction temperature. Finally, the *in situ* reaction was studied under autogenous conditions of high temperature where the conversion of ethanol to ethylene was rapid.

EXPERIMENTAL

The H–ZSM-5 samples used in this study were synthesized according to standard procedures described in a prior publication (*1*), and silicon and aluminum concentrations were measured by neutron activation. Two diffuse reflectance reactors were used in these studies, and both were obtained from Barnes Analytical/Spectra Tech (*2*). The first was a low-pressure cell using KBr windows which had temperature capabilities to 700°C and was used for most of the reactions described here. It was modified so that the cup which contained the heated sample had a thermocouple mounted directly in the powdered sample. The second reactor was a high-pressure cell which had temperature capabilities to 1100°C which used a single, domed crystal of zinc selenide and also contained a temperature probe located directly in the powdered zeolite. Both reactors were mounted in the DRIFT accessory (*7*) obtained from Spectra Tech. The reactors were built into a reaction manifold which had the capability to flow metered dry nitrogen gas containing varying concentrations of ethanol through the catalyst while the infrared spectra were monitored. The low-pressure diffuse reflectance reactor is illustrated in Fig. 1. The sample cup was equipped with a fritted disk so that reacting gases flowed into the top, down through the sample, and exited through the disk in the bottom. The cup was 0.082 in. deep and had an i.d. of 0.342

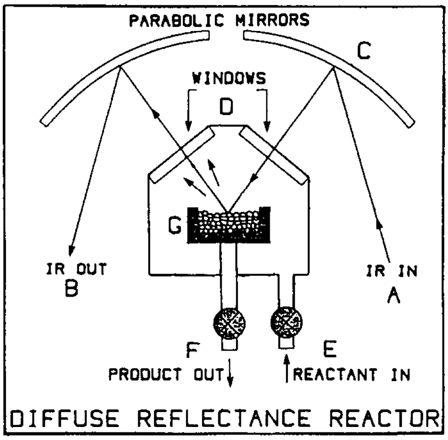

FIG. 1. Infrared diffuse reflectance reactor (*2*). The infrared beam (A) is directed toward parabolic mirrors (C) and focused through windows (D) onto the powdered sample contained in cup (G). The IR beam reflected from the sample passes out the opposite window onto the second parabolic mirror where it is refocused onto the detector. The gaseous reactants enter the reactor through port (E), pass downward through the catalyst in cup (G) and out a porous disk in the base of the cup, and exit through port (F). The low-pressure design uses KBr windows and the high-pressure cell uses a solid dome of zinc selenide secured by a high-pressure closure.

in. A thermocouple was mounted directly within the bed of the powdered catalyst. The total free volume of the cell was 1.5 ml.

The samples for infrared analyses were best diluted with powdered diamond at 10% concentration to ensure high-quality infrared spectra without distortions due to reststrahlen effects. Diamond powders were more useful generally than other materials since they were shown to be inert to the zeolite samples when studied to 500°C. Zinc selenide powders were found to give high-quality spectra and were inert when used to dilute samples studied below 200°C. All of the spectra reported here used the diamond powder dilution technique. The spectra were recorded on a Nicolet 60SX spectrometer using either an MCT-A or an MCT-B detector. The spectra reported were measured using 2000 to 5000 averaged scans taken at a spectral resolution of 4 cm^{-1}. No smoothing was applied to the displayed spectra unless specifically mentioned.

For spectra which measured zeolite samples reacting *in situ* with ethanol, where spectral ratioing was done to observe just the surface species, the spectra were ratioed to the pure, activated zeolite as background spectra recorded at the same temperature.

The pulse experiments were carried out under the following set of standardized conditions. A sample of zeolite diluted to a 10% (w/w) concentration in diamond powder was placed in the cup in the diffuse reflectance reactor and leveled with the top edge. Dry nitrogen at a gas hourly space velocity of 4390 hr^{-1} was flowed over the sample while it was heated slowly to 400°C. Infrared spectra continuously monitored the removal of water from the catalyst which was held at 400°C for a minimum of 4 hr. The sample was cooled to the lowest reaction temperature under the same flow of dry nitrogen where appropriate background spectra were recorded. Then pulses were made by flowing a 1.1% (v/v) ethanol in nitrogen stream over the catalyst at the initial reaction temperature until no further change was observed in the IR. A pure nitrogen stream (9.0 ml/min) was then flowed over the catalyst for 30 min. The infrared spectra for this initial set of conditions for the first temperature in the study were recorded. The catalyst was then heated under the flowing nitrogen stream at a heating rate of 2°C/min until the next desired temperature was reached and was constant for 30 min. Then the nitrogen flow was halted while an IR spectrum was collected over the next 10 to 20 min. This procedure enabled the observation of still adsorbed species as well as desorbed reactants and products. The flow of nitrogen was again started while the sample was heated to the next reaction temperature. Then the above-described IR measuring procedure was utilized to obtain spectra at each of the desired elevated temperatures.

The *in situ* reactions utilized samples of zeolites diluted in diamond powder and activated at 400°C as in the above-described pulse experiments. These samples were then cooled under nitrogen to the desired temperature and then continuously exposed to a flowing stream of 1.1% (v/v) ethanol in dry nitrogen (9 ml/min) while their infrared spectra were collected at each successively higher reaction temperature. These spectra were ratioed against the pure activated zeolite of appropriate Si/Al ratio at the subject reaction temperature for best observation of the reaction intermediates.

RESULTS AND DISCUSSION

Pure Materials Infrared Characterization

The infrared characterization of the zeolites used in this study demonstrated an interesting property of the silanols in the silicon-rich materials. The hydroxyl region of the infrared spectra for H–ZSM-5 samples between Si/Al of 35 and 1062 is shown in Fig. 2. The spectra were measured under a flowing stream of dry nitrogen at 400°C to eliminate distortions of the fundamental hydroxyl stretching region due to water ad-

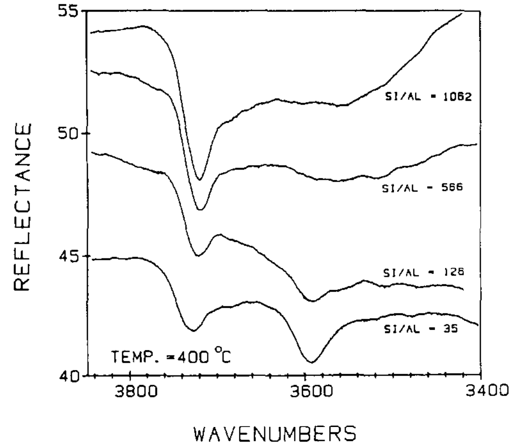

FIG. 2. Infrared spectra of the hydroxyl region measured at 400°C for H-ZSM-5 zeolites having Si/Al atom ratios of 35, 126, 566, and 1062 (number of data points used in smoothing algorithm = 17).

sorption. The aluminols and terminal silanols are clearly seen in the 35/1 material at 3605 and 3740 cm^{-1}, respectively. As the zeolites became more silicon rich, the Al(OH) frequency disappeared and the terminal silanol sharpened. The interesting aspect of these data was the observation of a broadband near 3500 cm^{-1} which became quite intense in the silicon-rich materials. These data are consistent with prior IR studies (*4*) measured under vacuum conditions which examined even higher Si/Al materials where the 3500-cm^{-1} band was assigned to hydrogen-bonded silanols. This assignment was supported by MAS NMR studies (*4*). The temperature-dependent infrared spectra of the material having a Si/Al atom ratio of 1062 are shown in Fig. 3. These spectra support the assignment of the 3500-cm^{-1} band to a hydrogen-bonded functionality in that as the temperature of the sample was increased, the intensity of the band decreased and the center of the peak position shifted from 3497 cm^{-1} at 60°C to 3536 cm^{-1} at 400°C. This behavior is typical of the thermal effects observed on hydrogen bonding of organic alcohols in solution. An interesting aspect of the data is the fact that the hydrogen-bonding interaction in the silanols persisted to very high temperatures. This suggests that they are rigidly located within the zeolites intracrystalline structure in near-neighbor positions, perhaps in silanol nests as suggested by Peri (*8*). Our data showed that the intensity and position of the hydrogen-bonded silanol varied with temperature reversibly as expected and were reproducible.

Ethanol Adsorption at Room Temperature

Zeolites having compositions of 126 and 1062 Si/Al ratios were reacted with ethanol at room temperature to compare the differences in their initial interaction with ethanol. The samples were first heated under flowing nitrogen at 400°C for 4 hr to drive off any adsorbed water before they were cooled in flowing dry nitrogen to ambient temperature in the diffuse reflectance reactor. The data shown in Fig. 4 for the 126/1 material show that ethanol reacted from a pulsed, diluted stream in nitrogen with the Al(OH) functionality rapidly and quantitatively at room temperature. The terminal silanols reacted only to a minor extent under these conditions after saturation of the sample with ethanol pulses. These data are

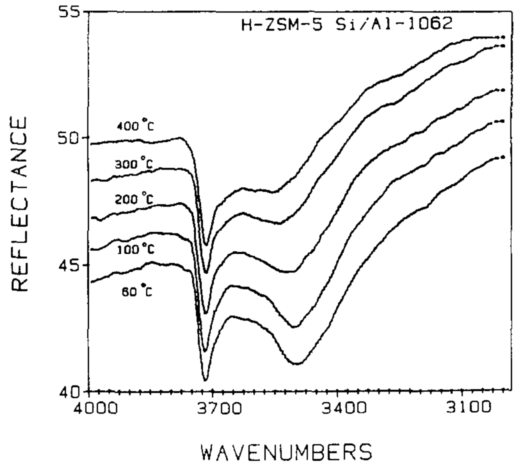

FIG. 3. Temperature-dependent infrared hydroxyl absorption near 3500 cm^{-1} for an H-ZSM-5 sample having a Si/Al atom ratio of 1062 at temperatures of 60, 100, 200, 300, and 400°C (number of data points used in smoothing algorithm = 17).

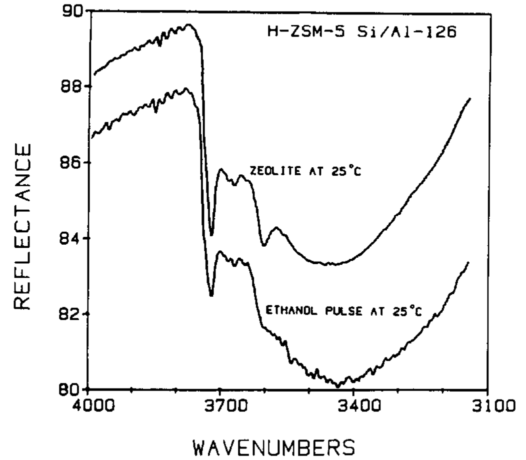

FIG. 4. Room temperature reaction of H–ZSM-5 having a Si/Al ratio of 126 with ethanol pulses. Top spectrum activated at 400°C and cooled to 25°C. Bottom spectrum after ethanol pulses at 25°C (number of data points used in smoothing algorithm = 9).

compared to the reactivity of the 1062/1 H–ZSM-5 illustrated in Fig. 5. The reactivity of the silicon-rich material in the figure shows that the terminal silanols in this material reacted at a moderate rate and were completely removed from the spectrum after successive pulses. The reactivity of the hydrogen-bonded silanols which appeared in the top spectrum in Fig. 5 near 3500 cm^{-1} was difficult to quantify since the ethanol which reacted with the sample gave rise to a very broad absorption in this same region. These results parallel those obtained for several other silicon-rich H–ZSM-5 compositions and indicate that both terminal and hydrogen-bonded silanols react with ethanol at room temperature. Upon heating of these samples to temperatures in the range 100–150°C the terminal silanol frequencies were restored at 3740 cm^{-1} for all of the zeolites studied.

These results provide an interesting contrast to the studies of Gorte and co-workers on the adsorption onto aluminum-rich H–ZSM-5 (Si/Al = 36) of methanol (*9*) and ethanol (*10*). Their studies showed that methanol adsorbed only reversibly at room temperature (*9*); ethanol mainly adsorbed reversibly along with a small fraction which irreversibly adsorbed which could be converted to ethylene at elevated temperatures (*10*). Their studies also demonstrated that 1 mole of methanol adsorbed per aluminum atom (*10*), and ethanol adsorbed in a 1.5/1 Al atom ratio (*10*). The IR studies reported here using aluminum-rich samples of Si/Al of 35 and 126 (Fig. 4) showed that ethanol adsorbed only to a minor extent onto the terminal silanol sites between 25 and 60°C, and part of the ethanol which irreversibly adsorbed onto the aluminum-based sites was converted to ethylene at elevated temperatures. In contrast to the aluminum-rich materials, the silicon-rich zeolites having Si/Al atom ratios greater than 500 reacted reversibly with the terminal silanol functionality at room temperature (Fig. 5, Si/Al = 1062), and this portion of the ethanol which adsorbed reversibly desorbed at 100°C. However, a portion of the ethanol which these silicon-rich zeolites adsorbed at room temperature was irreversibly adsorbed onto nonterminal silanol and nonaluminum-containing sites which was converted to ethylene when heated to 300°C.

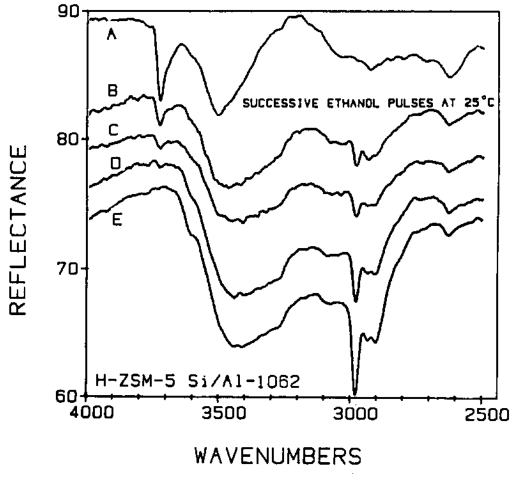

FIG. 5. Room temperature reaction of H–ZSM-5 having a Si/Al ratio of 1062 with ethanol pulses. Top spectrum (A) activated at 400°C and cooled to 25°C. Spectra B to E recorded after successive pulses of dilute ethanol stream in nitrogen at 25°C (number of data points used in smoothing algorithm = 17).

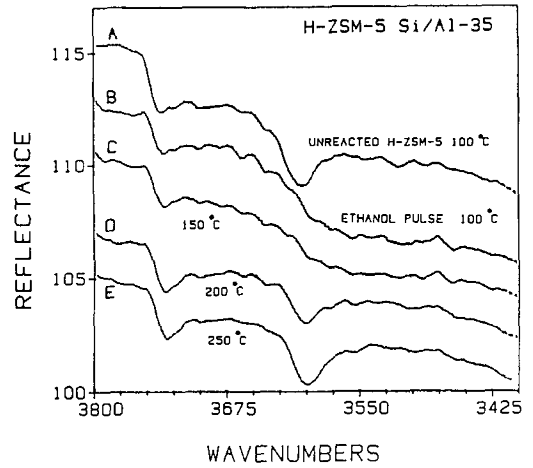

FIG. 6. Infrared in the hydroxyl region of H-ZSM-5 having a Si/Al ratio of 35, activated at 400°C and cooled to 100°C in IR spectrum A. Ethanol pulsed at 100°C until no further change in spectrum B followed by nitrogen flushing. Subsequent spectra were measured after heating in flowing nitrogen to 150°C in C, 200°C in D, and 250°C in E (number of data points used in smoothing algorithm = 11).

The thermolysis of ethanol adsorbed on these materials is discussed below and points to an interesting residual activity for silicon-rich zeolites. The low-temperature adsorption data suggest that the acidity of the terminal silanols increased as the aluminum concentration decreased to the point where they could reversibly adsorb ethanol in the silicon-rich materials.

Thermal Decomposition of Adsorbed Ethanol

To understand the sequence of steps by which the H-ZSM-5 catalysts convert ethanol to high-purity ethylene, a series of ethanol adsorbed zeolites was prepared and heated to elevated temperatures. For these experiments the H-ZSM-5 sample of 35/1 was compared to the 1062/1 material. The hydrogen-exchanged and dried samples of these zeolites were activated prior to reaction by heating to 400°C for 4 hr under flowing nitrogen. Then they were cooled under nitrogen to low temperatures (60–100°C) where pulses of ethanol in nitrogen were added until the aluminol-stretching frequencies disappeared from the spectra, and the silanols either disappeared or suffered no further change. These samples were then heated under flowing nitrogen to the specified temperature. At the end of this period the infrared spectra were measured with no nitrogen flow to record gas-phase products as well as surface-adsorbed species. Measuring the spectra also at the different temperature levels under a flow of nitrogen permitted the observation of just the adsorbed species.

The reaction sequence for the 35/1 material is shown in Fig. 6 for the hydroxyl region of the spectrum. These data show that when the zeolite was treated with ethanol at 100°C the terminal silanols were only slightly affected and increased in intensity only slightly when heated to 250°C. The aluminols disappeared entirely at 100°C when treated with ethanol; they reappeared in the spectrum at a temperature of 200°C and did not change very much when heated to 300°C. Figure 7 shows the surface alkoxyl and gas-phase ethylene region of the spectrum for this same material over the same temperature sequence illustrated in

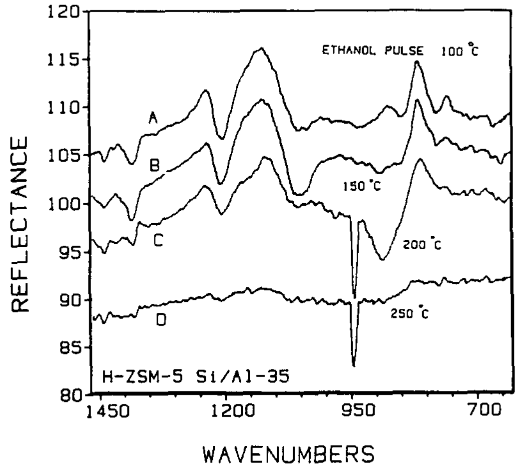

FIG. 7. Infrared in the fingerprint region of H-ZSM-5 having a Si/Al ratio of 35 treated with ethanol as in Fig. 6. Spectrum A recorded after ethanol pulses at 100°C. Chemisorbed ethanol decomposed at 150°C in B, 200°C in C, and 250°C in D (number of data points used in smoothing algorithm = 5).

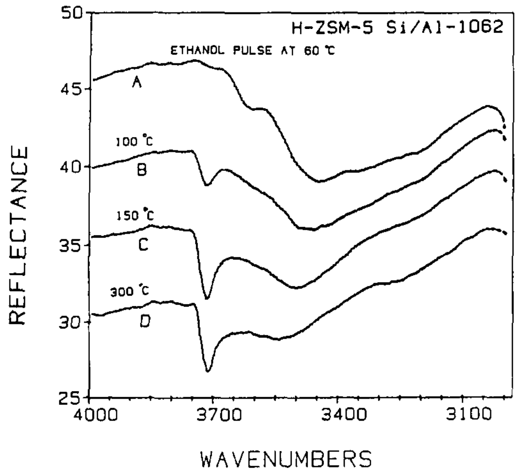

FIG. 8. Infrared in the hydroxyl region of H–ZSM-5 having a Si/Al atom ratio of 1062, activated at 400°C and cooled to 60°C where ethanol in flowing nitrogen was pulsed until no further change, giving spectrum A. The chemisorbed ethanol was then decomposed in flowing nitrogen at higher temperatures giving B at 100°C, C at 150°C, and D at 300°C (number of data points used in smoothing algorithm = 17).

the former figure. The key observation to gain from Fig. 7 is that ethylene appeared in the spectrum at 946 cm^{-1} only at 200°C, which was the same temperature required for restoring the aluminol to the spectrum for this composition shown in Fig. 6. The spectra obtained for this pulsed decomposition, as well as others on zeolites of differing Si/Al ratios, showed bands typical of those seen in Fig. 7 for surface-reacted ethanol. The data in this figure, as well as the next, were, for the purpose of this study, used mainly to specify the temperature at which ethylene was generated as a function of the silicon content.

A similar temperature-dependent study was carried out on the 1062/1 catalyst and is illustrated in Fig. 8. The hydroxyl region of the spectrum shows that the terminal silanols were completely removed by treatment with ethanol at 60°C and were fully restored to the spectrum when the sample was heated to 150°C. Although there were clearly changes in the hydrogen-bonded silanol region near 3500 cm^{-1} as a function of temperature, these changes could not be quantified with any confidence due to contributions to the spectrum in this region by adsorbed ethanol and product water as well as a temperature-dependent shift of the hydrogen-bonded silanols themselves. The key information to be obtained from these spectra is that the terminal silanols were fully restored at 150°C while Fig. 9, illustrating the fingerprint region, showed that ethylene did not appear in the spectrum until the 300°C temperature level had been reached. In contrast to the 35/1 catalyst which generated ethylene at 200°C, the IR studies showed that the silicon-rich material did not result in a decomposition to ethylene at 200°C.

From these pulse data we conclude the following: (i) The aluminols in the aluminum-rich materials reacted with ethanol in preference to the terminal silanols and decomposed at a low temperature near 200°C to simultaneously form ethylene and regenerate the Al(OH) site. (ii) Terminal silanols in silicon-rich materials reversibly adsorb ethanol rapidly even at low temperatures, but they decomposed at modest tempera-

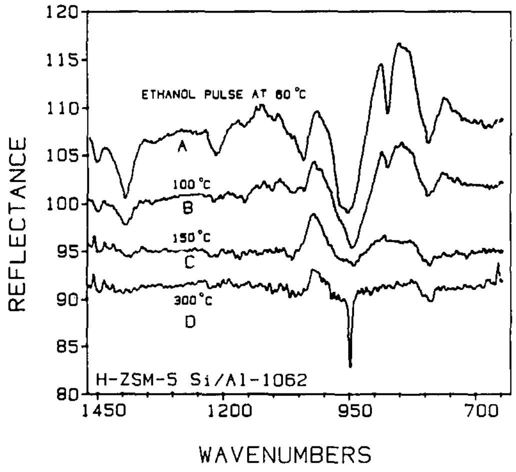

FIG. 9. Infrared in the fingerprint region of H–ZSM-5 having a Si/Al atom ratio of 1062 treated with ethanol as in Fig. 8. Spectrum A recorded after ethanol pulses at 60°C. Chemisorbed ethanol decomposed at 100°C in B, 150°C in C, and 300°C in D (number of data points used in smoothing algorithm = 5).

tures restoring the silanol functionality in the zeolite without conversion to ethylene. (iii) The terminal silanols in silicon-rich materials play no role in the catalytic conversion of ethanol to ethylene. (iv) The hydrogen-bonded silanols required a higher temperature near 300°C to produce ethylene. Thus, both the aluminum-rich catalysts, Si/Al of 35/1, and the silicon-rich materials, Si/Al of 1062/1, have acidic functionalities sufficient for the reaction with ethanol even at low temperatures, but the silicon-rich material requires a higher temperature to convert the chemisorbed ethanol to ethylene. These infrared data are entirely consistent with the flow reactor kinetic data reported in our other studies (*1*) which showed that the aluminum-rich materials were more active than the silicon-rich zeolites on a unit surface area basis. These studies do not permit the evaluation of the specific reactivity per active silanol site since their concentration could not be determined. Thus, no information on the relative reactivity of the active Si- and Al-based sites for ethanol dehydration could be generated.

Sodium Hydroxide-Exchanged H–ZSM-5

In the above-mentioned infrared studies, the difficulty was noted in quantifying the extent of reaction of the hydrogen-bonded silanols with ethanol due to the overlapping peaks from surface-reacted ethanol. To gain more conclusive information on the role of the hydrogen-bonded silanols in ethanol conversion to ethylene, the catalyst having a Si/Al atom ratio of 1062 was treated with 0.1 *N* NaOH at room temperature for 24 hr. In a separate paper (*1*), it was reported that the ethanol conversion rate using this catalyst before this treatment was rapid while the material after ion exchange was inactive. The infrared spectra for these two materials are shown in Fig. 10. The essential difference in the two spectra is the fact that the sodium hydroxide treatment mainly removed a portion of the hydrogen-bonded silanols from the spectrum which appear in the 3500 cm^{-1} region while having little effect on the terminal silanols. The ion exchange studies by Chester and co-workers at Mobil (*11*) showed that the degree of ion exchange in silicon-rich zeolites far exceeded the amount predicted by the ion exchangeable sites on the basis of the aluminum content of the material. The infrared data illustrated above indicate that the exchangeable sites are more acidic than the terminal silanols and that they reside in the hydrogen-bonded silanols. In combination with our catalytic data (*1*) these results support the proposal that the unexpectedly high ethanol dehydration activity in silicon-rich H–ZSM-5 zeolites is due to the acidity of a portion of the hydrogen-bonded silanols.

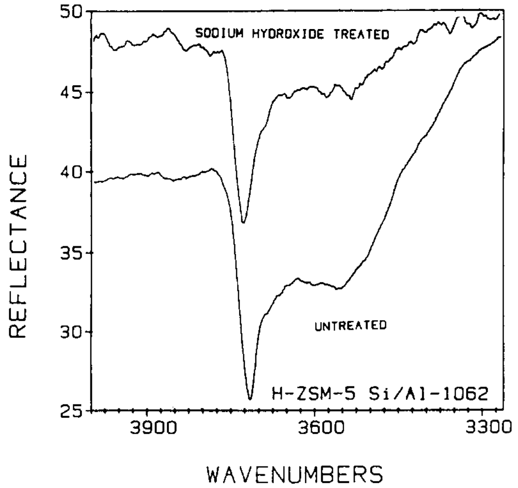

FIG. 10. Terminal and hydrogen-bonded silanols in H–ZSM-5 having a Si/Al atom ratio of 1062. Aqueous sodium hydroxide-treated material shown in the top spectrum and starting zeolite shown in the lower spectrum (number of data points used in smoothing algorithm = 5).

Infrared Studies under Autogenous Conditions

The *in situ* analysis of several compositions of H–ZSM-5 was studied as they catalyzed ethanol conversion to ethylene at high temperatures. These studies were examined in the diffuse reflectance reactor described under Experimental using a dilute

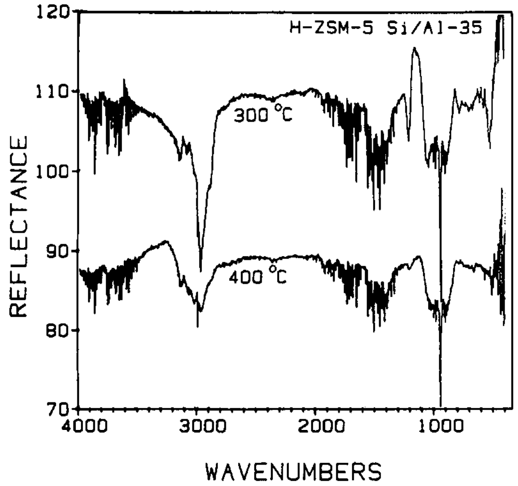

FIG. 11. *In situ* spectra at 300°C (top) and 400°C (lower) of H–ZSM-5 having a Si/Al atom ratio of 35 catalyzing ethanol conversion to ethylene from a dilute stream in nitrogen.

stream of ethanol in flowing nitrogen. The spectra in the accompanying figures illustrate the data for reactions at 300 and 400°C and were plotted without any smoothing. Figure 11 shows the data for the 35/1 catalyst. A key feature of the spectrum is the fact that ethanol conversion is quite high at both temperatures as indicated by only a trace of a band for ethanol near 1045 cm^{-1}. For the 566/1 and 1062/1 catalysts at 300°C, shown in Figs. 12 and 13, respectively, the ethanol band is moderately intense, but the conversion is near quantitative in the 400°C spectra. Ethylene appeared in all of these spectra as a sharp band near 946 cm^{-1}. It is noteworthy that the aluminum-rich 35/1 zeolite demonstrated a band in the *in situ* spectrum at 1214 cm^{-1} (Fig. 11) while the silicon-rich materials did not. This band is assigned to an aluminum ethoxide on the basis of the previously mentioned pulse studies on the 35/1 catalyst. These experiments demonstrated three IR absorption bands resulting from ethanol reacting with the surface at 1446, 1392, and 1214 cm^{-1}. That this assignment is correct was shown by the observation that when the ethanol-reacted sample was heated to 200°C, the AlOH band reappeared in the IR and all three of the alkoxy frequencies simultaneously disappeared. Greenler (*12*) reported the two high-frequency bands for aluminum ethoxide and ethanol adsorbed on alumina but did not report the 1212 absorption. Thus, the *in situ* spectra of the 35/

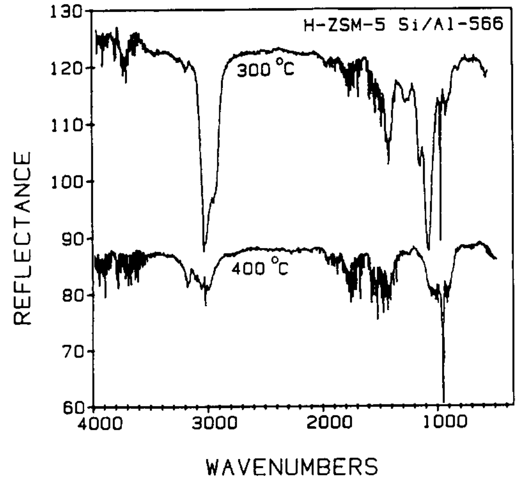

FIG. 12. *In situ* spectra at 300°C (top) and 400°C (lower) of H–ZSM-5 having a Si/Al atom ratio of 566 catalyzing ethanol conversion to ethylene from a dilute stream in nitrogen.

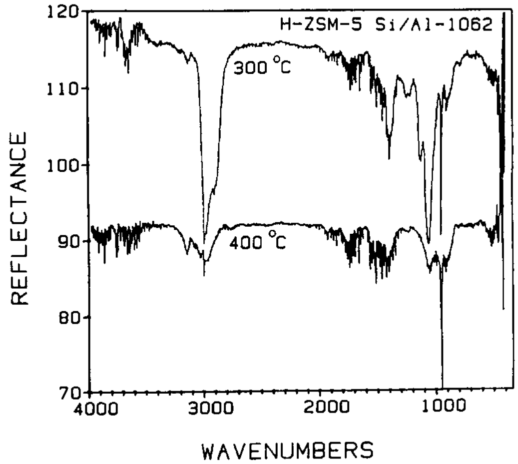

FIG. 13. *In situ* spectra at 300°C (top) and 400°C (lower) of H–ZSM-5 having a Si/Al atom ratio of 1062 catalyzing ethanol conversion to ethylene from a dilute stream in nitrogen.

1 material in Fig. 11 suggest that the aluminum-rich materials convert ethanol to ethylene through an aluminum alkoxide intermediate. That this intermediate is absent in the *in situ* spectra of the silicon-rich materials (Figs. 12 and 13) indicates that another catalytic mode is available to these materials. The weak absorption bands at 1245 and 1220 cm^{-1} in the 300°C spectra in Figs. 12 and 13 were due to unreacted ethanol. The pulse studies described before showed that the only strong absorption in the fingerprint region of the IR which resulted when ethanol reacted with the silicon-rich samples was a moderately broad absorption centered at 963 cm^{-1}. This frequency broadened upon heating and disappeared only above 300°C simultaneous to the generation of ethylene from the sample. Since pure ethylene was shown to react with the 1062/1 zeolite at 100°C producing a broad absorption band at 946 cm^{-1}, we conclude that the silicon-rich zeolites catalyze this reaction by converting ethanol to a strongly adsorbed ethylene at modest temperatures which is desorbed only above 300°C. Thus, the *in situ* spectra of the silicon-rich materials demonstrated only unreacted ethanol, a sharp band for ethylene, and a broad absorption under the ethylene peak centered at 945 cm^{-1} which we have assigned to adsorbed ethylene.

CONCLUSIONS

The catalytic conversion of ethanol to ethylene is promoted by aluminum-based Brønsted acid sites in the low-silicon regime of Si/Al atom ratios of 35/1 to 500/1. The silicon-rich zeolites having higher Si/Al atom ratios catalyze ethanol conversion to ethylene by Brønsted acid sites based on hydrogen-bonded silanols which are likely located in the intracrystalline structure as silanol nests (*8*). Increasing the silicon content in H–ZSM-5 led to an increase in the acidity of the terminal silanols so that these materials reversibly reacted with ethanol. A portion of the nested silanols within the intracrystalline structure of the silicon-rich zeolites was sufficiently acidic to reversibly adsorb ethanol and result in its dehydration to ethylene at elevated temperatures.

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