Silicon-Rich H–ZSM-5 Catalyzed Conversion of Aqueous Ethanol to Ethylene

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A study of the H–ZSM-5 catalysis of the conversion of aqueous ethanol solutions to ethylene was carried out using zeolites having Si/Al atom ratios of 35 to 15,000. Rates of ethanol conversion dropped sharply as expected until a Si/Al ratio of about 500; at higher ratios the activity was maintained at a nearly constant level. All of the synthesized zeolites afforded 100% conversion of 20% aqueous ethanol when examined at 400°C and space velocities (WHSV) of 3.4 hr^{-1} (based on the ethanol component). The ethylene selectivities steadily increased with the Si/Al ratio and reached a maximum of 99.6% using the silicon-rich H–ZSM-5 zeolites. The unusually high catalytic activity observed for the silicon-rich materials was attributed to especially reactive clusters of hydrogen-bonded silanols and was shown to be independent of the aluminum concentration.
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INTRODUCTION

Prior catalytic investigations of zeolites have principally examined strongly acidic materials with well-defined pore structures and relatively high aluminum concentrations. Catalytic reactions such as hydrocarbon cracking (*1*), conversion of oxygenates to aromatic gasoline (*2*), isomerization of aromatics (*3*), alkylaromatics disproportionation (*4*), and hydroisomerization (*5*) all require strongly acidic Brønsted sites centered on aluminum for their activity and have been well studied (*6*). Catalysis by highly siliceous zeolites has received limited attention in the prior literature (*7*) in general due to the expectation that the zeolites would be inactive for catalysis since they have few strong Brønsted acid sites centered on aluminum. Our reaction model suggested that certain reactions might be especially suited to catalysis by these materials. This report examines the efficacy of silicon-rich zeolites to catalyze one such reaction, the conversion of dilute aqueous ethanol to high-purity ethylene. Although it is well known (*8*) that the conversion of methanol to hydrocarbons by zeolites requires strongly acidic sites centered on aluminum, the less forcing ethanol dehydration reaction should in principle proceed through catalysis by a range of acidic sites, even mildly acidic ones. This assertion is supported by the observation of Jacobs (*9*) that the Y-type zeolite catalyzed removal of the elements of water from propanol forming propylene could be accomplished by a range of site acidities. Thus, the technology of methanol conversion to hydrocarbons by zeolites would be expected to be quite different from ethanol dehydration to ethylene where no molecular rearrangements or carbon–carbon bond formation is required.

This study examines the catalytic properties of H–ZSM-5 materials of Si/Al atom ratios of 35 to 15,000. The objective of the study was to understand the relationship between the intracrystalline properties and catalytic properties of such materials. The conversion of ethanol to ethylene, shown in Scheme 1, was especially suited to this study since it potentially provided a fundamental probe of the hydrophobic and acidic properties of the zeolite's intracrystalline structure. Through study of the change of ethanol conversion and ethylene selectivity as one systematically increased the Si/Al ratio, a better understanding of both their

19

$$CH_3CH_2OH \xrightarrow{\text{H-ZSM-5}} CH_2{=}CH_2 + H_2O$$
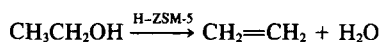
SCHEME 1

hydrophobic and residual acid properties was expected.

It followed from our conceptual model (12) that reaction rates would initially decrease with increasing Si/Al ratios due to the diminishing concentration of aluminum-based Brønsted acid sites, but they might increase as the Si/Al ratio increased to large values due to the expulsion of the product water from the system by the increasingly hydrophobic intracrystalline structure. It also suggested that the selectivity for ethylene formation should increase at the expense of higher hydrocarbon by-products, as the Si/Al ratio increased, because of the steadily declining AlOH, strongly acidic, Brønsted acid sites which are required for the conversion of ethylene to higher aliphatic and aromatic hydrocarbons (10).

The evidence that these materials are hydrophobic was given by Olson and co-workers (11) who showed that the water adsorption capacity of these materials decreased in a linear range over a wide composition of Si/Al atom ratios. Their catalytic studies on hexane cracking activity showed a linear decrease as the Si/Al ratios were increased.

The study of the conversion of fermentation alcohol-type solutions has additional importance in the development of a process for the conversion of biomass to basic chemicals. It was reported earlier (12) that even dilute aqueous ethanol solutions, as low as 20% by volume, were directly converted by certain zeolite catalysts to polymerization grade ethylene. This finding was important to the utilization of biomass since it could potentially eliminate the costly ethanol–water separation step (13) required in most fermentations to gasahol production.

EXPERIMENTAL

The zeolite catalysts used in these studies were either synthesized according to literature procedures (14) or obtained for purposes of comparison as development samples from commercial sources (15). The materials so obtained had Si/Al atom ratios between 35/1 and 15,000/1. Stirring the synthesis mixture was required in order to obtain H-ZSM-5 particles in the 3 to 5 μm range. Usually the sodium form of the zeolite was synthesized, calcined to remove the organic template, and subjected to a standard ion exchange technique using refluxing aqueous HCl. A slow, heat up calcination procedure in air over 6 hr to 530°C was utilized for the synthesis products. The samples were held at 530°C for 2 hr. The phase purity, crystallinity, and product identification were made using X-ray analysis. The silicon and aluminum contents of all of the samples reported were measured by inductively coupled arc plasma analysis using a Spectrametrics, Inc., Spectraspan 4 instrument and were verified by neutron activation analysis (16). Surface areas and diffuse reflectance infrared spectra were performed on all samples. Scanning electron microscopy (SEM) was used to monitor the size and morphology of the materials synthesized. In addition, particle size distributions were made using a Particle Data Electrozone Celloscope Model 80XY particle size analyzer. Pyridine and ammonia adsorptions were carried out and analyzed by infrared diffuse reflectance on selected samples to monitor the Brønsted and Lewis acid site concentrations (17), and FTIR analysis permitted the measurement of the relative amounts of the SiOH and AlOH moieties. The solid state MAS NMR measurements were performed by Dr. M. T. Melchoir of Exxon Research and Engineering Co.

The catalytic evaluation of the zeolites were carried out in an integral, microreactor using a sample size of 5–7 ml in an insulated electronically controlled furnace. The range of temperatures examined was 200 to 500°C, and the space velocities studied were in the range 0.2 to 8.0 hr^{-1} WHSV (on the basis of the ethanol component in the feed). A WHSV of 3.4 hr^{-1} was used for most studies; others are specified under Results and Discussion. The 20 to 95%

aqueous ethanol solutions were passed through a vaporizer before passing into the reactor section which was 0.5 in. in diameter. In most cases a small stream of nitrogen was metered into the reactor to serve as an internal gas chromatographic standard. The liquid feed was metered using precision micropumps with dampening facilities. Mass flow meters were used for the gas feed, and the gaseous product analysis was accomplished using an on-line gas chromatographic method. The process temperature of the endothermic reaction was measured by a thermocouple mounted directly in the catalyst bed. A sliding thermocouple in a thermowell monitored the axial temperature profile which in no case was greater than 10°C from inlet to outlet. A liquid collection system was used to collect the condensed product stream which was analyzed using an FID detector and n-propanol as an internal standard. This analysis determined concentrations of ethanol, higher alcohols, ether, acetaldehyde, aromatics, and higher hydrocarbons. The gases were analyzed by TCD where nitrogen was used as an internal standard to evaluate the ethylene concentrations. An FID analysis was used on the same stream to determine the concen-

tration of heavier products: propene, butenes, pentenes, acetaldehyde, and diethyl ether. A Porapak Q column was used for most analyses.

RESULTS

The studies reported here examined the rates and selectivities for ethylene formation as a function of H–ZSM-5 zeolites having Si/Al atom ratios of 35 to 15,000. This wide range of compositions permitted the examination of the catalytic properties of these zeolites of progressively increasing hydrophobic pore structures. In addition, results were obtained for varying ethanol concentrations in the feed, temperatures ranging from 200 to 500°C, and varying space velocities.

Compositional Effects on Conversion

The effects of the composition of H–ZSM-5 on the rates of conversion of 20% ethanol in water were studied from 200 to 500°C using Si/Al atom ratios of 35 to 15,000. The reactivity data as a function of the Si/Al ratio over this temperature range were quite unusual as illustrated by the study at 300°C shown in Fig. 1. Figure 1 plots the dehydration rate constants per
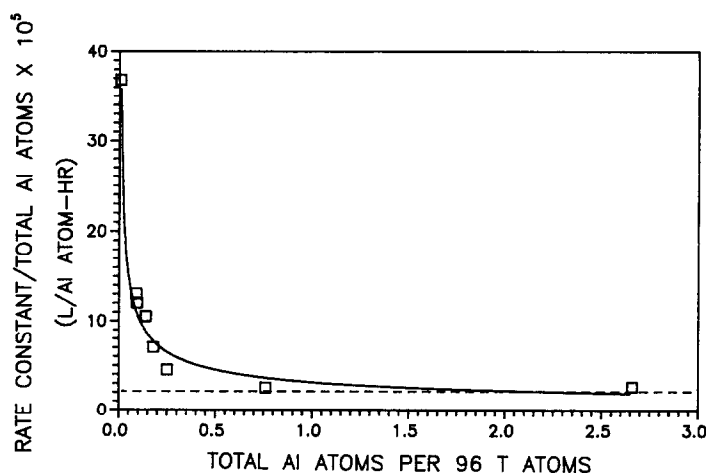

FIG. 1. H–ZSM-5 catalyzed reaction of 20% ethanol in water at 300°C by zeolites of Si/Al atom ratios of 35/1 to 15,000/1, WHSV = 3.4 hr^{-1}. The first-order rate constants on the ordinate have units of liters per total Al atoms per unit cell per hour. Kinetics were based on the total ethanol converted; ethylene selectivities were 60–75% depending on the Si/Al ratio where the balance was mainly diethyl ether.

aluminum atom versus the total number of aluminum atoms per unit cell for each zeolite sample. These data show that the reaction rates per Al atom were constant in the aluminum-rich region of Si/Al of 35 and 126, i.e., points at 2.67 and 0.76 Al atoms per unit cell, respectively. However, reactivity per aluminum atom became progressively higher in the silicon-rich regime below 0.5 Al atom per unit cell in the figure. For more forcing reactions like hexane catalytic cracking, activity is known (34) to be a linear function of the framework aluminum concentration. To examine this possibility for ethanol dehydration catalysis by H–ZSM-5, the framework aluminum concentrations were measure by solid-state ^{27}Al MAS NMR for several of the samples reported in Fig. 1. When these data were plotted in Fig. 2 as rate constants for dehydration per relative number of framework aluminum atoms in the samples versus the relative number of framework Al atoms per

unit cell, one observes that the reactivity was not dependent on the framework aluminum concentration in the silicon-rich regime. Had the dehydration activity been a function solely of the aluminum concentration, the plots in Figs. 1 and 2 would have given a horizontal line. Indeed, the aluminum-rich region of 2.76 and 0.76 Al atoms per unit cell in Fig. 1 shows a constant reaction rate constant per aluminum atom as indicated by the dashed horizontal line through these two points. This verifies that the dehydration activity in the aluminum-rich region is dominated by catalysis by aluminum. However, Figs. 1 and 2 also demonstrate that the silicon-rich region of 0.3 to near zero Al atoms per unit cell is much more reactive than expected based on aluminum contents. This region includes samples having Si/Al ratios in the range 500 to 15,000. The unusual aspect of these data is that the percentage ethanol conversions at 300°C did not continue to fall sharply in the silicon-rich regime but leveled off at a conversion of about 28% for the 1062/1 material and 11% for 15,000/1. A similar study at 400°C showed that all of the zeolite compositions from Si/Al atom ratios of 35 to 15,000 resulted in near quantitative conversions at a weight hour space velocity (WHSV) of 3.4 hr^{-1} (based on the ethanol component only). This illustrates that the silicon-rich samples are highly active catalysts for this reaction, and that their activity is unexpectedly high when judged from the point of view of the more forcing catalytic cracking reaction. The *in situ* infrared examination of these materials coupled with the data presented in this study suggests that the residual nonalumina dehydration activity arises from clustered silanol groups contained within the intracrystalline structure of the silicon-rich zeolites.

A comparison of the conversion data for the silicon-rich zeolites to a high-surface-area silica gel over the temperature range 360 to 500°C showed the latter to be substantially less reactive. A comparison of the rate constants at 360°C for silica gel to the
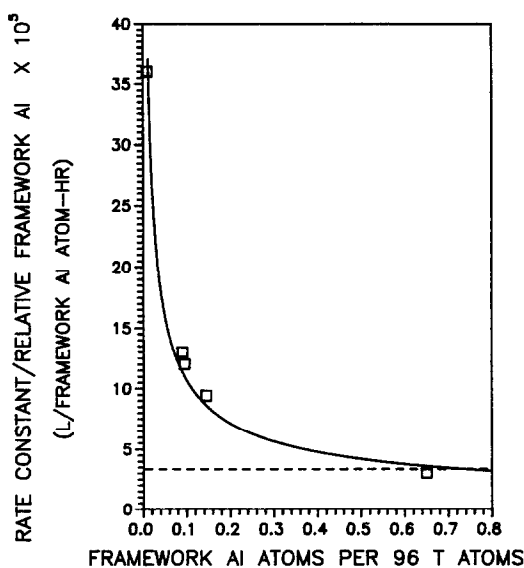

FIG. 2. H–ZSM-5 catalyzed reaction of 20% ethanol in water at 300°C by zeolites of Si/Al atom ratios of 35/1 to 15,000/1, WHSV = 3.4 hr^{-1}. The first-order rate constants on the ordinate have units of liters per relative number of Al framework atoms per unit cell per hour. The relative Al framework concentrations were measured by ^{27}Al MAS NMR.

silicon-rich H–ZSM-5 of Si/Al ratio of 1062 showed that the zeolite was more reactive by a factor of nearly 1000. A further dealumination of the 1062 catalyst by calcining in ambient air at 1000°C gave rise to a slight increase in ethanol conversion of 28.7 to 31.7% at 300°C.

Effect of Sodium Ion Exchange on Catalytic Activity

Evidence for hydrogen-bonded silanols, inside the H–ZSM-5 crystal, having a proposed structure of $Si(OH)(OSi)_3$ and $Si(OH)_2(OSi)_2$ was reported by Woolery and co-workers (18) and by Peri (19). Chester et al. (20) provided evidence for ion exchange properties of internal silanol groups. To determine whether these silanols were important in the silicon-rich H–ZSM-5 catalyzed ethanol conversion to ethylene, a sodium-exchanged form of the 1062 Si/Al material was prepared. The Si/Al 1062 H–ZSM-5 was treated with 0.10 N NaOH at room temperature for 24 hr. After water washing, the zeolite was slowly dried and examined for its ethanol conversion activity. A comparison of the reactivity of this Na–ZSM-5 form and H–ZSM-5 form of the 1062/1 catalyst showed that the sodium form was practically inactive, and a near quantitative conversion was obtained for the hydrogen form at 400°C using a WHSV of 3.4 hr^{-1}. The FTIR diffuse reflectance spectra (21) showed that the sodium exchange removed a large portion of the hydrogen-bonded silanols. These data suggested an unusual catalytic property of some of the intracrystalline silanols in the silicon-rich zeolites which is evaluated under Discussion.

Diffusional Effects on Catalytic Activity

To show that the unusually high and level activity for the H–ZSM-5 materials of Si/Al ratios of 566 and greater did not result from either an external or an internal zeolite crystal mass transfer effect, several studies were carried out.

The possibility of an external mass transfer limitation on the catalyzed rates was ex-

TABLE 1

Test for External Mass Transfer Limitation[a]

Temperature (°C)	Percentage ethanol conversion	
	Full bed	Half bed
400	97	96
355	78	82
300	28	27

[a] Inlet flow rates were adjusted so that contact times in all experiments were identical.

amined using the 1062 Si/Al catalyst in a full-bed reactor and compared to the results in a half-bed reactor where the linear velocity of the reactants passing over the catalyst was half that of the full-bed test while the contact times were held constant. Table 1 shows that the conversions observed at equal contact times were nearly identical at 300, 355, and 400°C.

The question of whether an intracrystalline mass transfer limitation might give rise to the unusual activity was examined in two ways. In the first case, there was no correlation between the measured mean particle sizes and the rates of ethanol conversion when a comparison was made for the entire series of H–ZSM-5 materials of Si/Al from 35 to 15,000. In other experiments, shown in Table 2, the 1062 Si/Al catalyst was separated into catalyst particles of mean sizes of 3.3 and 6.0 μm by repeated sedimentation

TABLE 2

Test for Intracrystalline Mass Transfer Limitation[a]

Temperature (°C)	Percentage ethanol conversion	
	3.29 μm	6.00 μm
400	96	99
355	86	86
300	31	31

[a] WHSV was 3.4 hr^{-1} using a 20% (v/v) ethanol in water feed.

experiments. The catalytic examination of this zeolite of two particle sizes for 20% aqueous ethanol conversion showed that there was essentially no difference in ethanol conversion activity under identical reactor conditions. Thus, the unusual ethanol conversion activity observed in Fig. 1 is likely centered on compositional effects.

In support of these conclusions, the possibility of diffusion-controlled catalytic reactivity was further examined by an Arrhenius treatment as seen in Fig. 3. The absence of any curvature in the resultant line in the figure over very rapid to very slow reaction regimes and the observation of an activation energy of 20.3 kcal/mole are both inconsistent with either an external or an internal diffusion limitation. The fact that the kinetics of the catalyzed conversion were first order with respect to ethanol was demonstrated by the data shown in Fig. 4. A linear correlation was obtained when the 1062/1 catalyst was used to convert a 20% (v/v) aqueous ethanol stream applying a standard plug flow intergral reactor design analysis. This development also permitted the computation of values of the rate constants shown in Figs. 1 and 2. Although the kinetics for alcohol conversions by zeolites in some cases demonstrate complex kinetics, clean first-order kinetics are usually
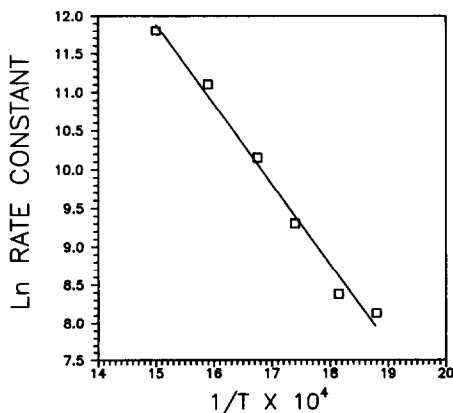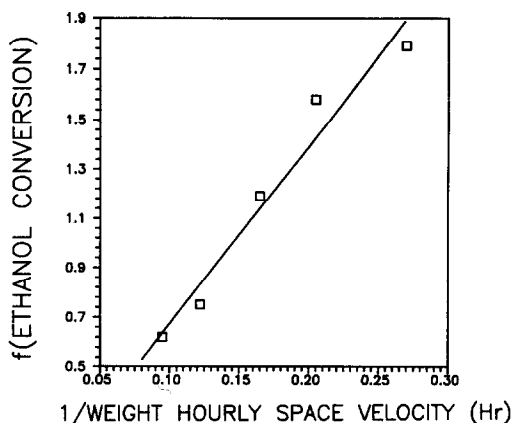

FIG. 4. First-order rate plot of contact time in hours (1/weight hourly space velocity, hr^{-1}) versus f(ethanol conversion, unitless) for a plug flow integral reactor for the conversion of 20% ethanol in water at 355°C using H–ZSM-5 of Si/Al = 1062. The f(ethanol conversion) = $(-[(1 + Y_A) \ln(1 - X_A) + X_A Y_A])$. X_A is the fractional conversion; Y_A is the fractional change in volume between 0 to 100% conversion. Kinetics were based on total ethanol converted; ethylene selectivities were greater than 90% for all points.

observed for the dehydration reaction when the products are olefins of corresponding carbon number (22). The kinetics of the elementary dehydration reaction of higher alcohols (22) and of ethanol reported here are in marked contrast to the autocatalytic nature observed in the conversion of methanol to hydrocarbons by Chen and Regan (23) involving a set of complex molecular transformations in the mechanism proposed by Dessau and LaPierre (24).

Compositional Effects on Ethylene Selectivity

Chang and Silvestri (25) first reported that an H–ZSM-5 catalyst having a low Si/Al atom ratio efficiently converted pure ethanol to a hydrocarbon mixture consisting mainly of isoparaffins and aromatics under conditions of low space velocities. Their work also showed that high space velocities resulted mainly in a light olefin mixture of principally ethylene and propylene. Furthermore, the selectivity to light olefins (8) over aromatics could be increased by
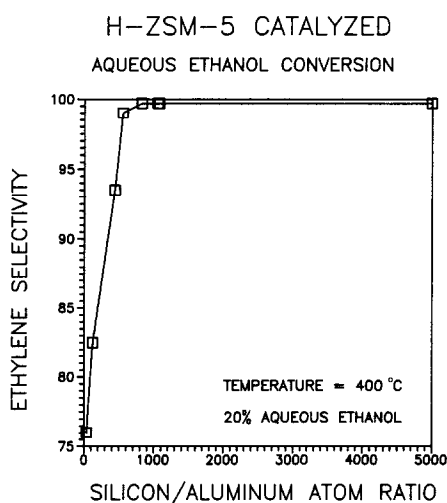

FIG. 3. Arrhenius plot, 1/temperature (K) versus logarithm of rate constants (hr^{-1}), for the conversion of 20% ethanol in water using H–ZSM-5 of Si/Al = 1062/1, WHSV = 3.4 hr^{-1}.

H–ZSM–5 CATALYZED

AQUEOUS ETHANOL CONVERSION

FIG. 5. Selectivity for ethylene formation from 20% ethanol in water at 400°C by zeolites of Si/Al atom ratios of 35/1 to 5000/1, WHSV = 3.4 hr^{-1}.

increasing the Si/Al ratio from 18 to 650. Oudejaris and van den Oosterkamp (26) examined an H–ZSM-5 of Si/Al atom ratio 45 for the conversion of aqueous ethanol and pure ethanol (50–100% ethanol) at low space velocities of 0.05 to 0.25 hr^{-1} and reported that the major products were materials in the gasoline range.

The data shown in Fig. 5 illustrate the ethylene product selectivities as a function of the Si/Al ratios under high conversion conditions near 100% at 400°C. Only in the case of the 35/1 catalyst were aromatics and higher isoparaffins formed. In contrast to the data on ethanol conversion rates as a function of Si/Al atom ratios in Fig. 1, the selectivity for ethylene formation seen in Fig. 5 steadily rose at the expense of by-products propene, butenes, and higher hydrocarbons. The observed selectivities for the catalysts of Si/Al of 1062 and greater at 98.5 to 99.5% conversions were within the polymerization grade ethylene range of 99.5% or better.

The lower olefin selectivities as a function of temperature for the Si/Al composition of 126/1 are illustrated in Fig. 6, and the 1062 catalyst data are shown in Fig. 7 for comparison. The principal reason for the increase in the ethylene selectivity at high temperatures was the suppression in propene and butene formation. Since these products require strong acid sites for their formation, the progressive increase in the ethylene selectivity with increasing Si/Al atom ratios was expected.
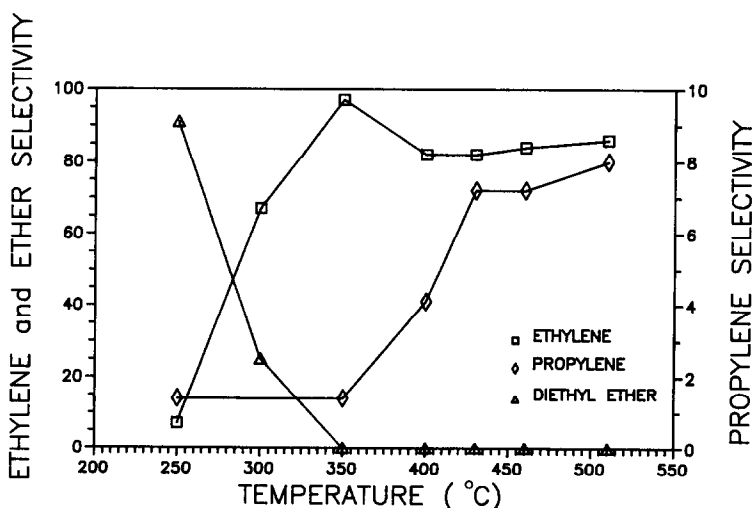
FIG. 6. Selectivity of products versus temperature for conversion of 20% ethanol in water by an H–ZSM-5 zeolite of Si/Al atom ratio of 126/1, WHSV = 3.4 hr^{-1}.
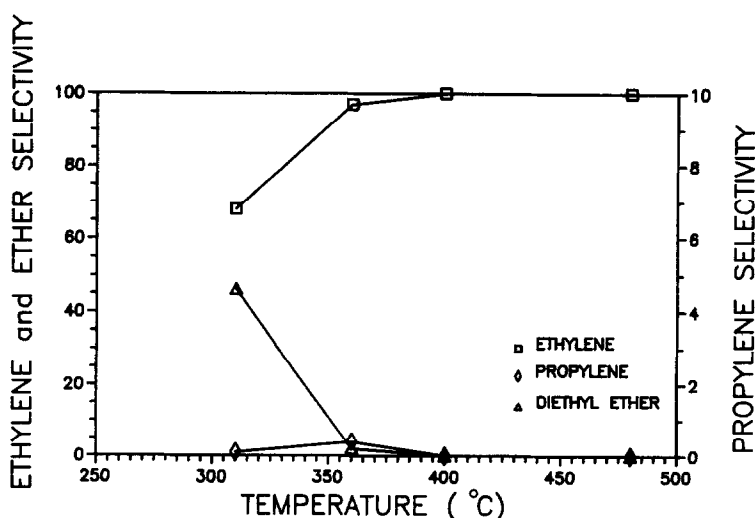
MOSER ET AL.

FIG. 7. Selectivity of products versus temperature for conversion of 20% ethanol in water by an H–ZSM-5 zeolite of Si/Al atom ratio of 1062/1, WHSV = 3.4 hr^{-1}.

Process Effects on Catalytic Activity

It was anticipated that zeolites of very low aluminum contents should provide high selectivities to ethylene even at very low space velocities, because of the small number of strong alumina-based acid sites. This idea was evaluated using an H–ZSM-5 catalyst having a Si/Al atom ratio of 1062 using a 20% aqueous ethanol feed stream at 400°C where the weight hourly space velocities were varied from 0.203 to 8.070 hr^{-1}. The reported space velocities here used only the ethanol component in the calculations for purposes of comparison to literature values. The data in Table 3 are shown to provide quantitative information on the conversions and total lower olefin selectivities. Figure 7 illustrates the very high ethylene selectivities observed using a silicon-rich zeolite even at very low space velocities which is unusual when compared to low Si/Al results using either ethanol (32) or methanol (8, 31).

The H–ZSM-5 catalyst of 1062 Si/Al ratio was used to examine the effects of water on ethylene selectivity at high conversions. These experiments compared a 95% aqueous ethanol solution to a 20% solution. At 400°C both gave high conversions of 99.6 and 97.3%, respectively. Their ethylene selectivities were 99.3 and 99.5%. Other experiments using the H–ZSM-5 material of 126 Si/Al atom ratio which produced by-product propylene in 4.2% selectivity showed little response to changes in selectivity when the ethanol in water concentration was varied using concentrations of 20 and 50%. Our data using 95% ethanol solu-

TABLE 3

Space Velocity Effects on Effluent Product Composition[a]

WHSV[b] (hr^{-1})	Effluent product composition (mole percentage)		
	Ethanol	Ethylene	Higher olefins
0.20	0.6	98.8	0.6
1.69	0.6	99.3	0.1
3.58	1.8	98.1	0.1
6.30	4.6	95.3	0.1
8.07	14.2	85.7	0.1

[a] Based on a 20% (v/v) ethanol in water feed at 400°C.
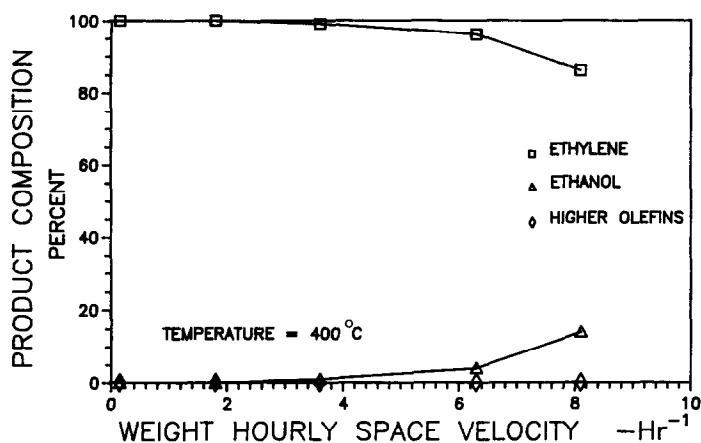[b] Weight hourly space velocity based on ethanol component of feed.

FIG. 8. Product composition versus weight hourly space velocity in hr^{-1} (WHSV = wt ethanol/wt catalyst/hr) for conversion of 20% ethanol in water at 400°C by an H–ZSM-5 zeolite of Si/Al atom ratio of 1062/1. Higher olefins observed were propene and butenes.

tions over the 1062/1 catalyst showed that high rates and excellent ethylene selectivities resulted, indicating that such catalysts may replace current processes employing alumina catalysts which require a 95% ethanol feed for ethylene production. X-ray analysis of these high-silica samples after as many as 60 hr on stream at 400°C using 20% aqueous ethanol showed no evidence for crystal destruction.

In the study of zeolite catalysts having Si/Al ratios of 1062 and higher, rates and selectivities did not diminish with time on stream. The samples usually changed color to slightly off white after 60 hr. A sample of the 126/1 catalyst was studied in a single reactor without recatalysis over an 8-month period using a variety of feed compositions, temperatures, and space velocities with a miniscule drop in activity. This catalyst was also a light tan color after more than 200 hr on stream.

DISCUSSION

Silicon to Aluminum Ratio Effects on Activity

To understand the relationship between the intracrystalline structure of the highly siliceous zeolites reported here and their catalytic properties for ethanol conversion,

one should examine an analogous reaction, the H–ZSM-5 catalyzed conversion of methanol to aliphatic and aromatic hydrocarbons. Chang and Silvestri (25) showed that H–ZSM-5 of relatively low Si/Al ratios catalyzed the conversion of methanol mainly to higher aliphatic and aromatic hydrocarbons which were appropriate for gasoline production. They showed that ethanol was converted to the same type of products only under conditions of low space velocity, and ethylene was formed only at very high space velocities. In contrast to the studies reported here, Chang et al. (8) showed that the methanol conversion activity of H–ZSM-5 catalysts of Si/Al atom ratios of 18 to 835 steadily declined as the ratio increased. Our data on aqueous ethanol conversion showed the same trend up to an Si/Al ratio of 444. As Fig. 1 illustrates, catalysts of higher Si/Al ratios in the range 566 to 15,000 showed a higher activity than expected, based on exclusive catalysis by aluminum, as the silicon content increased. This behavior is unusual since acid catalyzed reactions by zeolites generally lose activity in a linear fashion as the aluminum content decreases. The ethanol dehydration data presented here suggest that the decline in activity between Si/Al of 35 and

400 resulted from the decrease in the alumina-based acid sites, and that the moderately high level of activity at Si/Al above 400 resulted from nearly constant concentrations of sites which were still sufficiently acidic to promote ethanol dehydration.

The unusual aspect of the reactivity pattern shown in Fig. 1 is further emphasized by the observation of Auroux and co-workers (27) that not only the number of strong acid sites but also the total number of Brønsted and Lewis acid sites decreased when studied over an Si/Al atom ratio range of 18 to 60. Their heats of adsorption studies (27) also showed that the acid strength of the most acidic sites were much stronger in an H–ZSM-5 of low Si/Al atom ratio, but as the Si/Al ratio increased the proportion of the remaining sites in the zeolite which were strong acid sites increased.

When the highly siliceous zeolites were treated with 0.10 N NaOH at room temperature, the infrared studies (21) showed that a portion of the hydrogen-bonded silanols was preferentially removed, suggesting that certain structures of these silanols are more acidic than the terminal silanols. Since the ethanol conversion activity of the sodium ion exchanged catalyst was near zero, this indicates that certain hydrogen-bonded silanol moieties are responsible for alcohol dehydration while others are inactive. FTIR studies in these laboratories (12, 21) and in others (18) showed that hydrogen-bonded silanols are prominent in H–ZSM-5 materials with Si/Al atom ratios of 566 to 15,000. The fact that the ethanol conversion data were identical for two samples of the 1062 Si/Al catalyst of 3.3 and 6.0 μm mean particle sizes indicates that the active species is contained within the intracrystalline channels. Had the active site been located at the termination point of the crystal lattice either on the external surface or at the pore mouths, the reactivity of the smaller particle would have been greater since it contained a higher population of surface hydroxyls per unit mass due to its higher ratio of external to internal surface. This conclu-

sion is supported by the MAS NMR (18) data for these silanols. Using infrared data on hindered amine adsorption, Wu and collaborators (28) recently showed that the extracrystalline, terminal silanol concentration increased as the particle size decreased and that these silanols were mainly located in the external surface. That the dehydration is promoted by an especially reactive form of intraparticular Brønsted acid sites was supported by the observation that the conversion activity of a high-surface-area silica gel, containing a high surface hydroxyl content, was very low. In addition, the in situ infrared data (21) provided evidence that the terminal silanols in silicon-rich H–ZSM-5 were not responsible for ethanol conversion but the activity was due to the hydrogen-bonded silanol groups. The present studies also showed that ethanol conversion using H–ZSM-5 catalysts of low Si/Al ratios was principally effected via the strong Brønsted acid sites located on the aluminum atoms since activity dropped linearly with decreasing aluminum content in the aluminum-rich samples. This conclusion is supported by the studies of Aronson et al. (29) who demonstrated by TPD and TGA studies that alcohols generally adsorbed on aluminum-rich (Si/Al = 36) zeolites having stoichiometries of one alcohol molecule per aluminum atom, although the ethanol adsorption data was approximately 1.5/1. Our data do not permit an evaluation of the specific reactivity per aluminum-based acid site compared to that of the active hydrogen-bonded silanol site since the site concentration of the latter could not be determined.

Although our data do not directly relate to the role of Lewis acid sites in promoting ethanol conversion, the fact that the catalytic activity was destroyed by sodium ion exchange which specifically reacted with the hydrogen-bonded silanols suggests that the activity is more reasonably attributed to a Brønsted acid site mechanism. The question of the importance of Lewis acidity was addressed by examining the catalytic activ-

ity of the 1062 Si/Al H–ZSM-5 both before and after high-temperature calcining. A sample of this catalyst was calcined in ambient air at 1000°C for 12 hr. According to the results of Vedrine and co-workers (30), thermal treatment of H–ZSM-5 materials to 802°C resulted in a modest decrease in the Brønsted acid site concentration, but the Lewis acid site population substantially increased. A comparison at 300°C of the catalytic activity for the conversion of ethanol to ethylene from a 20% aqueous ethanol solution showed that the 1000°C calcined catalyst experienced only a 10.5% increase in rate. If the prior literature (30) is correct in concluding that this type of calcination leads to greatly increased Lewis acid sites, the magnitude of the alteration of the catalytic activity does not seem consistent with Lewis acid sites responsible for catalysis. Rather, this type of calcination in ambient air is known to remove framework aluminum reducing the strong Brønsted acidity of the material. The fact that the high-temperature calcination resulted in only a small rate change, and the ethylene selectivity slightly increased, suggests that the principal effect was one of dealumination of the sample.

Silicon to Aluminum Ratio Effects on Selectivity

The conversion of both aqueous and pure ethanol over the H–ZSM-5 catalysts of high Si/Al ratios reported here led to ethylene in high selectivities at 400°C as shown in Fig. 5. Lower temperatures resulted in more diethyl ether and high temperatures above 450°C led to small increases in the acetaldehyde and lower olefin production.

Inspection of the ethylene selectivity trend as a function of the Si/Al content in Fig. 5 indicates that the observed selectivities are in accord with expectations based on the decreasing Brønsted, strong acid site concentration as the ratio increases. In studies directed toward a methanol to lower olefins process, Chang and co-workers (8) showed that methanol conversions using

H–ZSM-5 catalysts having Si/Al ratios of 18 to 835 resulted in progressively more light olefins in the C2 to C5 range as the Si/Al ratio increased. However, their results showed a continuous decrease in methanol conversion with an increase in the Si/Al ratio. Kaeding (31) also showed that a higher selectivity to lower olefins resulted from methanol with H–ZSM-5 catalysts of high Si/Al atom ratios. Derouane and co-workers (32) compared both methanol and ethanol conversions to mainly aromatics and higher aliphatics using an H–ZSM-5 with an Si/Al ratio of 22 and concluded that both reactions proceeded by basically the same strong acid catalyzed mechanism. It was reported (8) for methanol catalysis that when the Si/Al ratio in H–ZSM-5 was held constant at 35 while the Na/Al ratio was varied over a wide range, the catalysts having the highest acidity were the least selective toward ethylene and lower olefins. Extensive studies by Choudhary and Nayak (7) clearly demonstrated the requirement of aluminum atoms in the unit cell and strong acid sites for the production of aromatics. Their studies showed that the acid sites in H–silicalites of Si/Al ratios near 10,000 were mostly weakly acidic and would not catalyze aromatization. They also provided evidence (33) that only the strong acid sites in H–ZSM-5 which irreversibly adsorbed pyridine above 653 K convert ethanol to aromatics.

Although the near linear increase in ethylene selectivities observed over the Si/Al range of 35 to 804 (Fig. 5) was not at all surprising, based on the methanol studies mentioned above, the observation of very high selectivities above 99.6% ethylene was noteworthy.

Mechanistic Model

Clearly, the rate versus the concentration of Al atoms per unit cell in Fig. 1 cannot be rationalized solely in terms of strong Al-based acid site concentrations. The conversion rates in the low Si/Al regime of 35/1 to 126/1 were likely dominated by aluminum-

based, strong Brønsted acid sites as indicated by our *in situ* FTIR data (21) and supported by Fig. 1. A replot of the data in Fig. 1 in the form of dehydration rate vs Si/Al ratio shows a nearly linear decrease in the rate in the aluminum-rich region, i.e., Si/Al of 35–400, which parallels the decline in activity (11) in catalytic cracking. These data lead to the conclusion that the ethanol conversions for the 1062/1 and 15,000/1 catalyst should have been near zero by a simple extrapolation of the low Si/Al conversion data if only AlOH sites were important. The maintenance of rates in the silicon-rich materials is an interesting phenomenon and likely resulted from especially reactive silanol functionalities as was indicated by the IR data (21).

The MAS NMR studies of Woolery and co-workers (18) showed that there were only two types of silanols in silicon-rich H–ZSM-5 and they have the structures Si(OH)(SiO)$_3$ and Si(OH)$_2$(SiO)$_2$. Their data do not address the question of nested silanols (19). Our infrared data (21) showed that hydrogen-bonded silanols in the silicon-rich zeolites were readily exchangeable by sodium hydroxide. Since sodium ion exchange and stabilization by chelation would be more favorable using Si(OH)$_2$(SiO)$_2$ than Si(OH)(SiO)$_3$, we assign the active and most acidic silanol groups for ethanol conversion in the silicon-rich regime to either Si(OH)$_2$(SiO)$_2$ structures or silanol nests (19) composed of several Si(OH)(SiO)$_3$ groups which could also stabilize sodium ion exchange by chelation.

At the outset of this paper, it was suggested that the increasing hydrophobicity which ZSM-5 experienced as the Si/Al ratio increased (11) might lead to an enhanced rate of ethanol dehydration due to the increasing expulsion of water from the dehydration equilibrium. A second alternate explanation to the hydrogen-bonded silanol model proposed above for the maintenance of the high ethanol conversion rates at high Si/Al ratios could be increased ethanol concentration within the channel as the zeolite becomes more silicon-rich, which would increase the rate of a first-order reaction. This effect could be counterbalanced under the given reaction conditions by the expected continuous rate decline due to the decreasing concentration of aluminum-based acid sites. Although both of these mechanisms could contribute to the activity of this system at high silicon concentrations, we consider the infrared evidence (21) and the reactivity and selectivity data reported in this paper directly supportive of the silanol site reactivity model. Accordingly, we conclude that the hydrogen-bonded silanols within the intracrystalline structure of ZSM-5 are sufficiently acidic to promote the mild acid catalyzed dehydration of ethanol to form ethylene.

The conclusion that ethanol dehydration by silicon-rich H–ZSM-5 is promoted by intracrystalline silanol nests instead of aluminum-based Brønsted acid sites runs contrary to expectations based on alkane conversions by these same catalysts. Haag *et al.* reported (34) that the rate constants for hexane and 1-hexene cracking and 1-hexene double-bond isomerization decreased linearly with total aluminum content when studied on H–ZSM-5 samples having Si/Al ratios of 35 to greater than 20,000. They further showed that hexane cracking activity was directly related to the concentration of framework aluminum atoms in the samples. Their data comparing hexane cracking and 1-hexene isomerization showed that the latter reaction rate was 10^6 faster than the cracking rate. Consequently, an exceedingly low number of aluminum atoms could give rise to a substantial overall conversion if isomerization activity were to be based exclusively on catalysis by aluminum. Thus, it is possible that in the ethanol dehydration studies reported here, the activity was due to trace amounts of framework aluminum atoms. However, in addition to the infrared evidence previously described (21), the data shown in Figs. 1 and 2 suggest that this is not the case. These graphs clearly show

that the reactivity per aluminum atom increases in a regular fashion as the aluminum content decreases. The dashed line in each graph indicates the expected reactivity had the dehydration been catalyzed by acid sites exclusively associated with the aluminum atoms in the samples. The studies on hydrocarbon conversions cited above (34) indicate that the reactivity per framework aluminum site does not increase to any significant degree as the framework aluminum content decreases. Thus, if there were a slight increase in the acidity of each aluminum-based acid site as the silicon content increased, the change in acidity was not so great as to have any effect on the specific catalytic activity. Consequently, we conclude that the increase in the dehydration activity shown in Fig. 2 per framework Al atom did not arise from any increase in aluminum atom-based acidity as the silicon content increased. The data suggest that the silicon-rich samples contain sites, sufficiently acidic to catalyze the mild dehydration reaction, not based on aluminum. The infrared data (21) suggest that the residual activity of the silicon-rich zeolites is due to moderately acidic internal silanols.

CONCLUSIONS

Fermentation-type alcohol solutions containing 20% aqueous ethanol were readily converted to polymerization grade ethylene by silicon-rich H–ZSM-5 zeolites. The low Si/Al catalysts converted ethanol mainly by strong acid sites based on AlOH groups. Silicon-rich H–ZSM-5 catalyzed ethanol conversion to ethylene by way of hydrogen-bonded silanol sites which may be located within the intracrystalline structure as silanol nests and may involve structural units like $Si(OH)_2(SiO)_2$. The high selectivities observed for ethylene production, greater than 99.6% using the silicon-rich materials, resulted from the absence of strong Brønsted acid sites in the intracrystalline structure. The data permitted no definitive conclusion regarding the effects of

hydrophobic intracrystalline channels on reaction rates for dehydration reactions.

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MOSER ET AL.

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