A Temperature-Programmed Desorption Study of Olefin Oligomerization in H–ZSM-5[1]

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We have used temperature-programmed desorption and thermogravimetric analysis (TPD-TGA), with gas chromatographic analysis of products, to examine the low-temperature reaction of ethene, propene, and 2-methyl-2-propanol in H–ZSM-5. Propene reacts rapidly inside the zeolite at 295 K to form large oligomer chains, while the zeolite must be heated to above 370 K for ethene oligomerization to occur. In both cases, reaction does not stop until a coverage of 7.8 g/100 g is reached on a zeolite with a SiO_2/Al_2O_3 ratio of 70. This is a substantial fraction of the zeolite pore volume, >50% assuming that the density of the oligomers is similar to that of polypropylene, suggesting that reaction stops only when blocking prevents reactants from approaching the acid sites. In TPD carried out under vacuum, the oligomer chains from both ethene and propene are completely removed in two desorption features centered at 420 and 550 K. Analyses of the products from both ethene and propene show a similar mixture of olefin products ranging from C_2 to C_7, with no noticeable preference for monomer, dimer, or trimer products. Analysis of the butene isomers in the products indicates that the concentrations are close to that obtained for equilibrium mixtures. With 2-methyl-2-propanol, adsorption and dehydration occur at 295 K. On a zeolite sample with a SiO_2/Al_2O_3 ratio of 70, concentrations of the olefin desorption products formed in TPD are essentially identical to those observed for propene and ethene, suggesting that they are due to the formation and cracking of oligomeric species very similar to that observed following olefin adsorption. On a zeolite with a SiO_2/Al_2O_3 ratio of 520, this oligomerization with 2-methyl-2-propanol can be minimized and methylpropene is a major product. These results are discussed in relation to previous studies of oligomerization and alcohol dehydration reactions. © 1989 Academic Press, Inc.

INTRODUCTION

In a series of recent papers, our research group has examined the acid sites in H–ZSM-5 and other high-silica zeolites by studying the adsorption and desorption of adsorbates which can undergo simple, acid-catalyzed reactions (1–8). The main result of this work was to show that these materials contain a collection of identical acid sites in a concentration of one per framework Al atom. For the simple alcohols, 2-propanamine, and 2-propanone, 1 : 1 adsorption complexes were formed at these Al sites; and the reactivity of these complexes was independent of SiO_2/Al_2O_3 ratio

and zeolite structure for H–ZSM-5, H–ZSM-12, and H–mordenite (3, 6, 7). The products observed in temperature-programmed desorption (TPD) of 2-methyl-2-propanol from this 1 : 1 state under ultra-high vacuum showed that oligomerization of the butene formed by dehydration of this alcohol was more rapid than diffusion of the butene out of the zeolite pores except for zeolites with very high SiO_2/Al_2O_3 ratios (3, 6). Furthermore, for small olefins like propene, 1 : 1 adsorption complexes could not be formed since propene was found to oligomerize rapidly at 295 K, even at pressures below a few Torr (2, 9). The apparatus used in all of this prior work, however, did not allow a detailed analysis of the products in the desorption of propene or 2-methyl-2-propanol.

In this paper, we will report the results from a more detailed examination of the

products formed in TPD under ultrahigh vacuum following adsorption of ethene, propene, and 2-methyl-2-propanol in a H–ZSM-5 zeolite. The results show that the temperature range for desorption and the products obtained are essentially the same for each of the adsorbates. For each of the adsorbates, the range of products includes mainly olefins between C_2 and C_7; and the relative amounts of each of the four butene isomers are found to be close to the equilibrium concentration. These results imply that the same intermediates are formed in the zeolite following the adsorption of ethene, propene, and 2-methyl-2-propanol and that the products observed in desorption are due to sequential cracking of these intermediates into smaller products. These results will be discussed in the context of previous reaction studies of olefin oligomerization to help explain what species are present in the zeolite cavities under reaction conditions.

EXPERIMENTAL TECHNIQUES

The apparatus used in these experiments was the TPD-TGA system used in previous papers, with the addition of a gas chromatograph (6, 7). It consisted of a Cahn 2000 microbalance which could be evacuated with a turbomolecular pump to a base pressure below 1×10^{-7} Torr. The system pressure during adsorption was monitored by a capacitance manometer, and a Spectramass quadrupole mass spectrometer was attached to the chamber for monitoring partial pressures during evacuation and desorption. Approximately 17 mg of zeolite was spread over a flat sample pan on the microbalance to avoid bed effects in adsorption and desorption (10). The heating rate for the TPD-TGA experiments was maintained at 10 K/min, and a thermocouple placed near the sample was used for temperature measurement. In the TPD experiments, the mass spectrometer was interfaced with a microcomputer so that several mass peaks could be monitored simultaneously.

Our previous work has shown that a number of hydrocarbon products can be formed during adsorption of 2-methyl-2-propanol or simple olefins (2, 3). Due to the difficulty of differentiating these hydrocarbon products in TPD with the mass spectrometer, the gas chromatograph was added to the system. To perform a chromatographic analysis of species desorbing from the zeolite, samples were exposed to the adsorbate of interest, evacuated, and isolated from the turbopump and the mass spectrometer. The sample temperature was then ramped in the usual way and the gas-phase products were collected in a $\frac{1}{2}$-in., stainless-steel tube immersed in liquid nitrogen. The products could be collected in any given temperature range during the TPD-TGA experiment. Following the desorption event of interest, the stainless-steel tube was isolated from the system; and the products were transferred to a gas-sampling valve on the GC by warming the stainless-steel tube and immersing the loop from the sampling valve in liquid nitrogen. Chromatograms were measured using a column containing 80/120 Carbopack B 3% SP-1500 packing supplied by Supelco, Inc., and a flame ionization detector. Retention times and sensitivity factors for various products were determined using known standards; however, due to the large number of products observed, we did not attempt to identify all of the isomers which were formed.

The use of a cold trap to evacuate the sample and collect desorbing products was checked in separate experiments and appeared to have little affect on either the desorption temperatures or the products detected. No pressure rise was observed using the capacitance manometer during a TPD-TGA experiment with the cold trap being used as a pump. Also, TGA results using either the turbopump or the cold trap to pump the system, shown in Fig. 1 for propene adsorption, were virtually identical. To test the ability of the trap to collect all products formed on the zeolite, a known
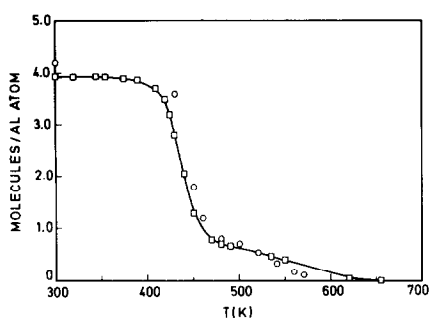
FIG. 1. TGA results following propene adsorption on H–ZSM-using the turbomolecular pump or the cold trap to evacuate the system. The results are virtually identical and demonstrate that the use of the cold trap for evacuation of the zeolite and sample collection is unlikely to affect the products observed in our experiments.

mixture of ethene, pentene-2, and octene-1 was admitted into the empty system in the gas phase at the pressures which would be obtained from desorption without evacuation and a sample was collected with the cold trap. The results demonstrated that the trap was capable of evacuating the system and collecting a representative sample from an olefin mixture.

The zeolite samples were initially saturated with the compound of interest by exposing the zeolite sample to approximately 15 Torr of the adsorbate until no further weight gain was observed. Propene and 2-methyl-2-propanol adsorbed rapidly on the zeolite at 295 K, and the exposure used for these adsorbates was 5 min. However, ethene adsorption was prohibitively slow at 295 K (9, 11–13). To adsorb ethene, the sample temperature was raised at 10 K/min, while the sample was exposed to 15 Torr of ethene, until rapid adsorption was observed. Rapid adsorption began at approximately 370 K. The sample temperature was then held at 400 K until no further weight gain was recorded before being cooled to 295 K. All of the desorption measurements were obtained following evacuation of the sample to remove most of the weakly adsorbed material. Over the course

of an experimental sequence involving one adsorption/desorption cycle, the total mass change in the zeolite sample was found to be negligible for each of the adsorbates examined, indicating that no residual products were left undetected in the zeolite.

The zeolite samples with SiO_2/Al_2O_3 ratios of 70 and 520 were obtained as NH_4–ZSM-5 powders from the Mobil Oil Co. and will be designated ZSM-5(70) and ZSM-5(520) in this paper. Electron microscopy indicated that the zeolite particles were uniformly between 0.4 and 0.5 μm in diameter, and X-ray diffraction of these samples agreed with the published data for ZSM-5 (14). The Al content in these samples was checked using ^{27}Al NMR of the hydrated samples, with an aqueous solution of $Al(NO_3)_3$ as a reference (15). For all of the experiments reported in this paper, the hydrogen form of the zeolite was prepared by heating NH_4–ZSM-5 to 700 K under vacuum. The H–ZSM-5(70) used for most of the experiments in this paper was further characterized by exposing it to 15 Torr of n-hexane, resulting in an uptake of 12.4 g/100 g of zeolite. Assuming a liquid density for the adsorbed n-hexane, this coverage corresponds to 0.18 cm^3 n-hexane/g of zeolite which is close to the porosity of ideal ZSM-5.

RESULTS

The TGA-TPD results for 2-methyl-2-propanol, propene, and ethene on H–ZSM-5 are shown in Figs. 2–4. The results for 2-methyl-2-propanol have been discussed in detail previously and will be only briefly summarized here (3). On H–ZSM-5(70), the weight change following exposure to the alcohol for 5 min and evacuation for 6 h corresponds to slightly more than one butene molecule per Al. Following the TPD-TGA experiment, the sample weight returns to its original value. Mostly olefin products (m/e = 41) are observed desorbing in peaks at 420 and 540 K, with no unreacted alcohol (m/e = 45) and only a small amount of water (m/e = 18) being observed. While a peak
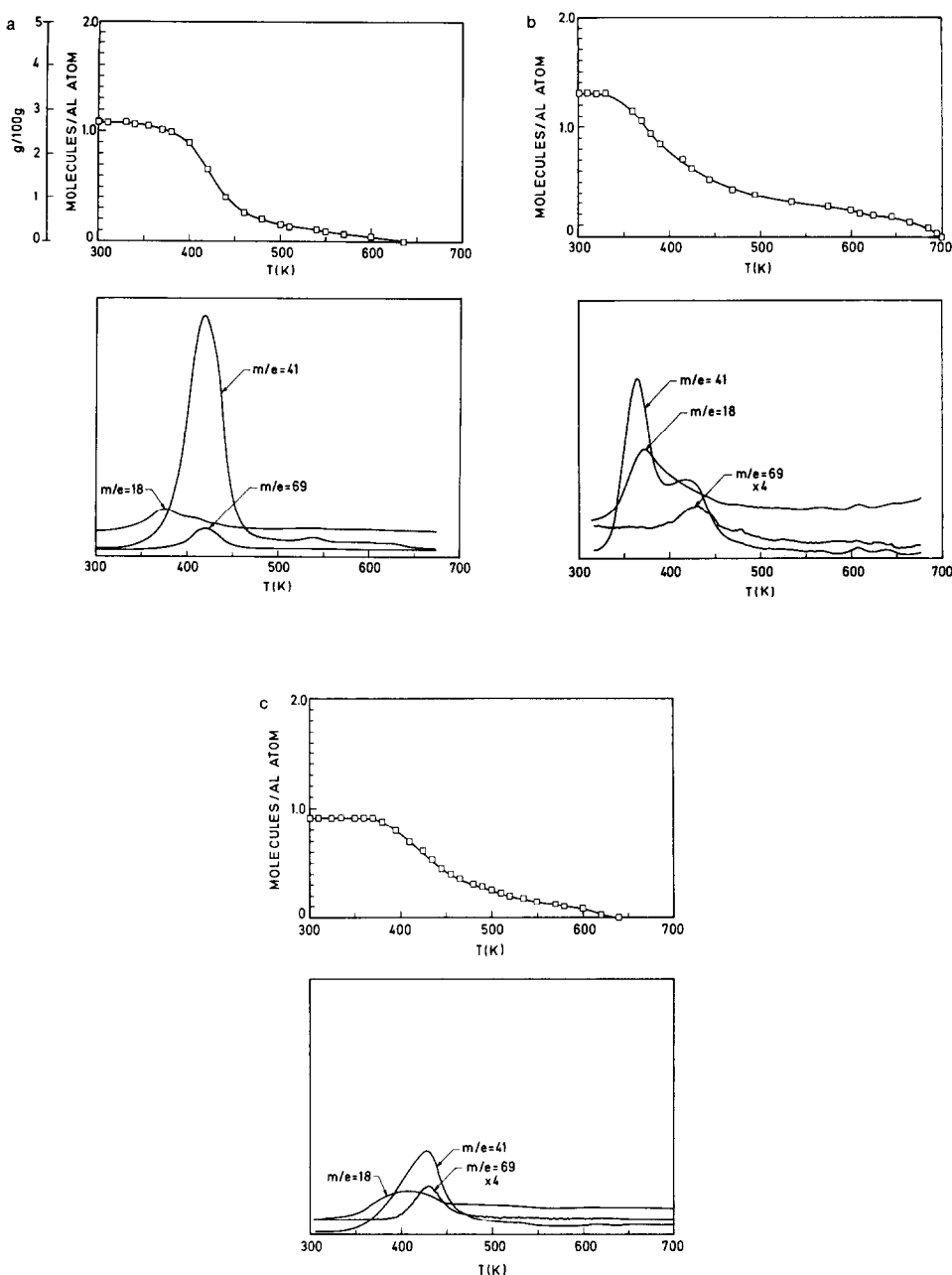
FIG. 2. TPD-TGA results, using the mass spectrometer, following adsorption of 2-methyl-2-propanol on (a) H–ZSM-5(70), following evacuation for 6 h; (b) H–ZSM-5(520), following evacuation for 3 h; and (c) H–ZSM-5(520), following evacuation for 20 h. No unreacted alcohol was ever observed in TPD on any of the samples. On H–ZSM-5(70), only a small amount of water (m/e = 18) was observed, indicating that dehydration and subsequent removal of water occur during the evacuation procedure at 295 K. The olefin products desorbing from this sample at 420 K (m/e = 41 and 69) contain olefins larger than butene, as indicated by the presence of the peak at m/e = 69. On H–ZSM-5(520), the olefin desorption feature (m/e = 41) at 370 K does not contain larger olefin products, as shown by the absence of a feature at the same temperature for m/e = 69. These monomeric species can be removed by prolonged evacuation.
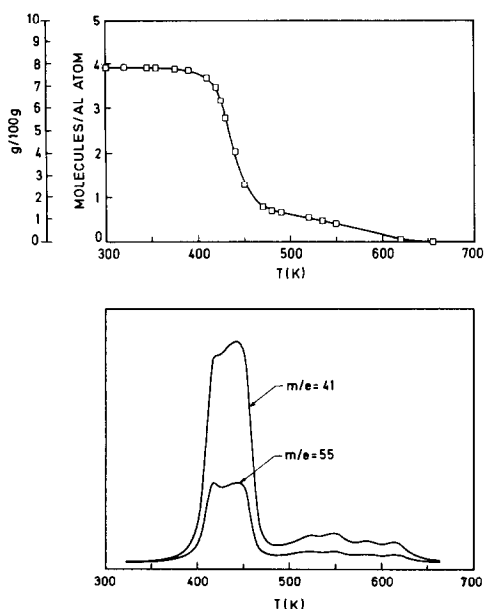
FIG. 3. TPD-TGA results following exposure of H–ZSM-5(70) to 15 Torr of propene for 5 min at 295 K. All of the products formed by propene are removed from the zeolite by heating. The olefin products (m/e = 41 and 55) contain species larger than propene, as shown by the presence of the peak at m/e = 55.

TGA results for the H–ZSM-5(520) sample in Figs. 2b and 2c. Figure 2b was obtained following exposure to 2-methyl-2-propanol and evacuation for 3 h. No unreacted alcohol desorbs from the sample, but the olefin products monitored using m/e = 41 show an additional low-temperature maximum near 360 K. However, the products desorbing in this feature do not exhibit a peak at m/e = 69, indicating that oligomer products are probably not present in this feature. The results in Fig. 2c were obtained on the same sample as that in Fig. 2b, but the data were collected after 20 h of evacuation. After this longer evacuation period, the desorption feature at 360 K is not observed, showing that the intermediates which decomposed to form butene on the H–ZSM-5(520) sample could be removed from the sample by evacuation. We were also able to observe butene with the mass spectrometer during this evacuation period. The desorption fea-
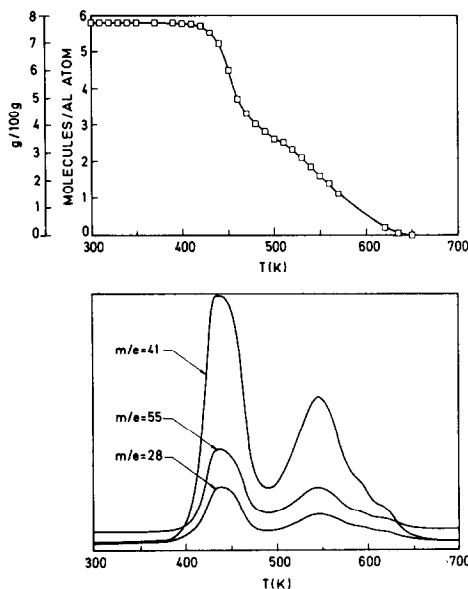
at m/e = 41 in the mass spectrum is present for most olefins larger than propene, at least some of the olefin products were larger than butene, as indicated by the presence of a peak at m/e = 69 in the mass spectrum of the products. The results imply that 2-methyl-2-propanol reacts on the acid sites at room temperature and that the water produced by dehydration is removed during evacuation along with the alcohol in excess of one per Al. The presence of higher molecular weight species indicates that the butene molecules formed in the dehydration reaction undergo secondary reactions before leaving the zeolite pores.

Our results indicate that, upon adsorption of 2-methyl-2-propanol, the stoichiometry is one butene molecule per Al site. Since dimerization requires two olefin molecules, the importance of secondary oligomerization reactions is a function of the acid-site density. This is shown in the TPD-

FIG. 4. TPD-TGA results following exposure of H–ZSM-5(70) to ethene using the dosing procedure described in the text. All of the products are removed from the zeolite by heating. The olefin products (m/e = 28, 41, and 55) contain species larger than ethene, as shown by the presence of the peaks at m/e = 41 and 55.

ture at 420 K on both Figs. 2b and 2c must be due to butene molecules which undergo oligomerization prior to leaving the zeolite and, therefore, cannot be removed from the zeolite until higher temperatures. This is consistent with recent ^{13}C NMR results which have also shown the importance of secondary reactions upon adsorption of 2-methyl-2-propanol, even at room temperature (16).

Our TPD-TGA results for propene and ethene are shown in Figs. 3 and 4, respectively. For propene, the initial weight change following exposure of the H–ZSM-5(70) sample of 15 Torr of propene for 5 min, followed by evacuation, corresponds to 7.8 g/100 g zeolite or ~4 molecules/Al atom. Assuming a density for the adsorbate of 0.9 g/cm^3, a number typical for poly-propylene, this coverage corresponds to greater than 50% filling of the zeolite pore volume by the oligomers. TPD shows that most of this adsorbed material is removed in desorption features centered at approximately 430 and 550 K. (The multiple features in both peaks appear to be due to fluctuations in the sample heating rate.) We did not observe peaks at $m/e = 65$ or 91 (simple aromatics) or at $m/e = 43$ or 29 (aliphatic compounds) in the mass spectrum of the products, implying that most of the products were olefins. Both TPD features in Fig. 3 occur well above the temperature at which propene desorbed from H–ZSM-5 following 2-propanol adsorption (405 K) (3); and peaks were present at $m/e = 55$ and 69 in the mass spectrum of the products, implying that at least some of the products were larger than propene. This is consistent with what has been reported previously (2, 9, 11) and indicates that propene readily oli-gomerizes on H–ZSM-5 at room temperature.

Ethene also oligomerizes on H–ZSM-5, but higher temperatures are necessary to initiate the reaction. For adsorption at room temperature, only physically adsorbed ethene was present in the zeolite and this ethene could be easily removed by

evacuation. The TPD-TGA curves in Fig. 4 were obtained following the adsorption procedures described under Experimental Techniques and involved exposure to ethene at 400 K for 30 min, cooling to 295 K, and evacuation for 15 h. The sample weight increase was essentially identical to that observed for propene adsorption at 295 K, 7.8 g/100 g (~6 molecules/Al). This similarity to propene is probably due to the fact that, in both cases, reaction stops only after the zeolite pore volume surrounding the acid sites is substantially filled. The higher temperatures required for ethene than for propene are due to the fact that the second-ary carbocations formed by protonation of propene are energetically more accessible than the primary carbocations which must be formed by ethene (3). The TPD-TGA results for ethene are similar to those for propene and 2-methyl-2-propanol, with the exception that the TPD feature centered at 550 K is proportionally larger for ethene.

To identify the species observed in TPD, samples of desorbing material were collected and analyzed by GC in the manner described earlier, with the results for the 430 K desorption peak for each adsorbate shown in Fig. 5a. Over 70 peaks were observed in the chromatograms for each of the product distributions, although most products formed were in the C$_2$ to C$_7$ range. No compounds larger than C$_{10}$ were found in detectable quantities, even though separate tests showed that our methods of sample collection were capable of observing larger products. While the selectivity of 2-methyl-2-propanol to form butenes was slightly higher than the selectivity of propene and ethene to form butenes and while somewhat more ethene was observed on the sample saturated with ethene, the product distributions following exposure to all three adsorbates are remarkably similar. This, along with the fact that desorption occurred in the same temperature range for all three adsorbates, points toward a common intermediate in each case.

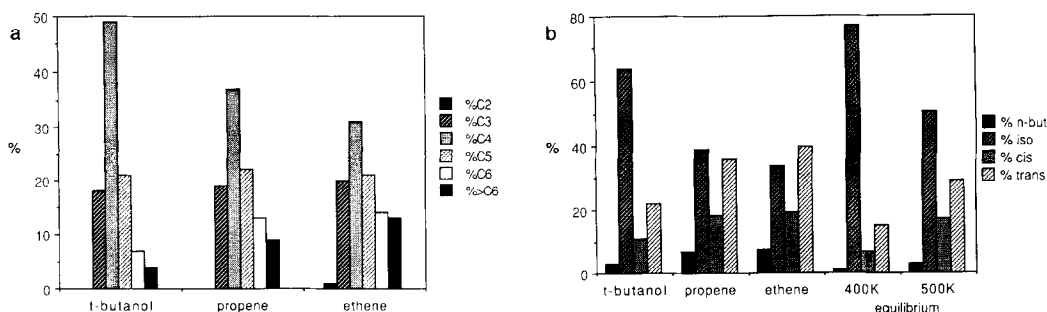The fact that the products formed are not

FIG. 5. A comparison of olefin products collected during desorption between 300 and 500 K, using the gas chromatograph, for 2-methyl-2-propanol, propene, and ethene on H–ZSM-5(70). In (a), the product distribution is shown for each of the adsorbates. In (b), the isomer distribution of the four butene products is shown to be close to that observed for equilibrium at these temperatures.

simple dimers, trimers, etc., of the olefins originally exposed to the zeolite implies that the products are actually formed by cracking of large, oligomeric chains. That long chains are formed in the zeolite has been indicated previously by spectroscopic investigations. In ^{13}C NMR studies of ethene, propene, and 2-methyl propene on H–ZSM-5 (11), the only peaks observed were due to carbon atoms in saturated, aliphatic molecules. Since the reaction of olefins to oligomers must result in at least one terminating carbon (a carbenium ion, a carbon covalently bonded to oxygen, or two olefinic carbons) per chain unless hydride transfer occurs, the fact that no other NMR peaks were observed in this previous study implies chains which are so long that peaks due to terminating carbons are too small to be detected. However, the use of cross polarization in the NMR study may have exaggerated the relative size of the alkyl carbon peaks. This increase with cross polarization in the relative sizes of alkyl versus terminating carbons is due to different relaxation times for the different carbon species and has been observed for propene oligomers in an H–Y zeolite (17). Cracking in the beta position from a carbenium ion center on this chain could explain the wide distribution of products observed for each of the adsorbates and the similarity in that distribution for ethene and propene. [13]C

NMR spectra following adsorption of labeled 2-methyl-2-propanol ($(CH_3)_3$[13]COH) on H–ZSM also show peaks in the region observed for saturated carbon atoms, and the chemical shifts and relative intensities of these peaks are essentially identical to that observed following adsorption of olefins (16). Therefore, the similarity in the product distributions for all three adsorbates is not unreasonable.

Previous reactor studies of olefin oligomerization on H–ZSM-5 have shown that the product distributions typically approach that expected from thermodynamic, equilibrium considerations (18, 19). Since pressure in the zeolite pores during desorption is not well defined in our experiments, we examined selectivity ratios for the different butene isomers formed by each of the adsorbates and compared them to the equilibrium ratios at 400 and 500 K, with the results shown in Fig. 5b. For all three adsorbates, a similar mixture of the four butene isomers was observed. It is interesting to note that simple dehydration of 2-methyl-2-propanol should lead to methylpropene while linear butenes could only be formed from the monomeric t-butyl group if rearrangement occurred. Rearrangement via a carbenium ion would require the transformation of a tertiary ion to a primary ion, and this process would not be expected to be fast at these temperatures
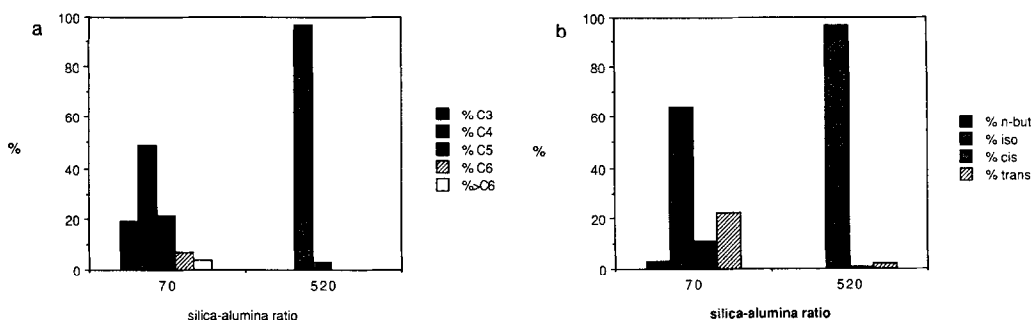
FIG. 6. A comparison of the product distribution (a) and butene isomer distribution (b) collected during desorption for 2-methyl-2-propanol on H–ZSM-5(70) and H–ZSM-5(520). Only products desorbing below 395 K were collected on the H–ZSM-5(520) sample, corresponding to the low-temperature olefin feature in the TPD curve of Fig. 2b. Methylpropene is the only product observed in this desorption feature on H–ZSM-5(520), implying that no oligomerization or subsequent cracking occurs at low temperatures on this sample.

(20). While the butene isomer formed in the largest concentration from 2-methyl-2-propanol was methylpropene, the isomer concentration ratio for the products actually lies between that expected for equilibria at 400 and 500 K. It seems likely that most of the butenes are formed by cracking of oligomers and not simple dehydration. The butene products obtained from propene and ethene have a slightly higher percentage of linear species than would be expected from equilibrium, but this is probably related to size constraints in the zeolite cavities.

Further evidence that much of the butene formed is due to cracking oligomers and not by simple dehydration is presented in Fig. 6. Here, the product distribution for the low-temperature desorption feature (360 K) for 2-methyl-2-propanol on the H–ZSM-5(520) sample is compared to the product distribution on H–ZSM-5(70). As we stated in our discussion of Fig. 2b, there is no evidence for secondary oligomerization reactions in the mass spectrum for this desorption feature. The GC results confirm this conclusion. There is also no evidence for isomerization of the butyl group, since essentially all of the desorbing product is methylpropene.

We also investigated the origin of the second, high-temperature desorption feature which was present for each of the adsorbates but was most important following ethene adsorption. We compared the composition of the desorbing products and the butene isomer distribution for the two peaks in ethene desorption, with the results shown in Fig. 7. Differences in the product distributions for the two peaks do not appear to be significant. This raises the question of why there should be two oligomer decomposition processes, occurring at different temperatures, which result in similar products. Our conjecture is that the 430 K feature in TPD is due to cracking of an unsaturated chain, whereas the 550 K feature is due to the cracking of a saturated chain formed by interchain, hydride transfer. Higher temperatures are needed to form the carbenium ions from saturated molecules, which then undergo the same cracking chemistry found on the unsaturated chains. Hydrocracking of alkanes on H–ZSM-5 has, in fact, been observed to occur at temperatures only slightly higher than 550 K in reactor environments (21). While H_2 or methane is likely to be formed in the initiation step of this reaction (21), these would be difficult to detect in our experiments and could be in very low concentrations. If aromatics are formed in the hydride transfer, these may be removed during evacuation
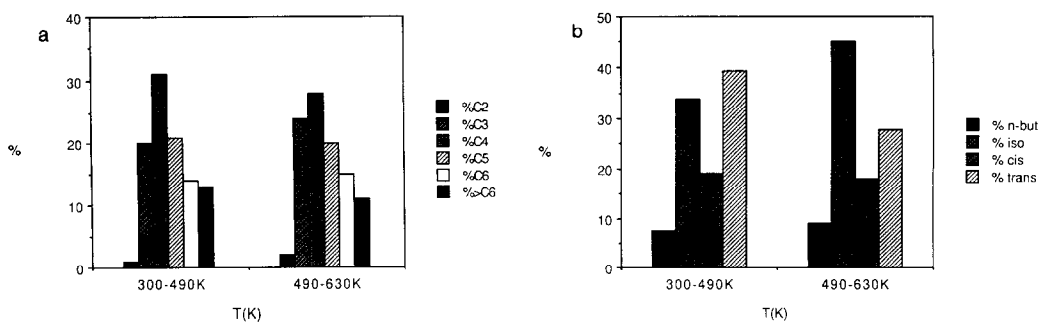
FIG. 7. A comparison of olefin products formed in the two desorption features (see Fig. 4) observed following ethene adsorption in H–ZSM-5. Samples were collected during desorption in the temperature ranges 300 to 490 K and 490 to 630 K. The similarity in the product distributions for both temperature ranges suggests that the same chemical processes are responsible for both desorption features. The high-temperature feature is likely due to cracking of oligomer chains which have become saturated by hydride transfer.

prior to performing a TPD experiment. Studies of toluene adsorption on H–ZSM-5 have proven that simple aromatics can be removed under the conditions of our experiments (5). The reason for the 550 K feature being more prominent for ethene can probably be explained by the fact that higher temperatures were needed for adsorption of ethene and this would be expected to facilitate the interchain, hydride-transfer reactions necessary for producing the saturated chains.

DISCUSSION

It is clear that the oligomerization and cracking chemistry which we have reported in this paper are carbenium ion reactions. The product distributions are consistent with that reported for hydrocarbon cracking and olefin oligomerization reactions (18, 19, 22, 23), both of which are well known to occur through carbenium ion intermediates. Our adsorption studies show that these olefin oligomerization and catalytic cracking reactions can occur readily at low temperatures and pressures in high-silica zeolites and that the oligomeric chains formed in the zeolite under adsorption conditions can lead to the products observed in reaction studies.

As discussed earlier, each oligomer chain in the zeolite must contain a double bond, a carbenium ion center, or a covalent, silyl ether linkage to the zeolite framework, unless hydride transfer from another adsorbate has occurred to saturate the chain. While UV (24) and ^{13}C NMR (25) spectroscopic studies have given evidence for carbenium ions following propene adsorption in H–Y and H–ZSM-5 zeolites, more recent ^{13}C NMR studies have suggested that the stable form of the catalytically important center is a silyl ether (or alkoxide) species in which the proton from the Al site is transferred to the olefinic molecule and the resulting alkyl group is covalently bonded to the framework oxygen of the zeolite lattice (15–17). This species is probably in equilibrium with the analogous carbenium ion which is responsible for the observed chemistry.

The extent of branching for the oligomer chains remains unknown. One of the earlier mentioned ^{13}C NMR studies of olefins in H–ZSM-5 reported that the chains formed by ethene, propene, and methylpropene inside the zeolite appeared to be linear, based on the assignment of peaks in the alkyl carbon region to CH_3, CH_2, etc., groups (11). However, it should be noted that there is a considerable range of chemical shifts possible in ^{13}C NMR for the different types of

carbon atoms, even in simple alkanes (26), and it is probably not possible to assign peaks in the spectrum to a specific type of alkyl carbon. This implies that the oligomers may actually be highly branched, as should be expected since the oligomers will be formed by a carbenium ion mechanism. It is interesting to note, however, that the ^{13}C NMR spectra for the oligomers formed by each of the olefins are very similar, implying that the oligomer chains are independent of the adsorbate used to form them. This may help to explain the identical uptakes for ethene and propene and the very similar distributions which we observe in the cracking products for each of the different adsorbates. Finally, while the differences in product distributions obtained following adsorption of ethene, propene, and 2-methyl-2-propanol in our study are not large, the product distributions are not the same, indicating that there may be subtle differences between the chains formed by each of the adsorbates.

Our results do give insight into some of the chemistry occurring under normal reaction conditions. For example, it appears that a substantial fraction of the pore volume of the zeolite is likely to be filled with oligomer chains when olefin reactions are carried out at temperatures below 500 K, conditions which reaction studies show lead to simple dimer, trimer, etc., product distributions rather than the more complex mixture obtained by cracking of the adsorbate alkyl groups (18, 22, 23). This implies that a product distribution of simple oligomers is due to reaction on the external surface of the zeolite. At higher temperatures, it seems reasonable that the growing and cracking of chains are competing processes which lead to the wide product distributions which are observed. Even in reactions such as methanol to olefins, there is evidence that these growing chains could be present (27). Also, the terminating center of the chains, which undergoes carbenium-ion-like chemistry, may react with neighboring alcohol molecules in the initial dehy-

dration step for these alcohol reactions, explaining the autocatalytic effects which are frequently observed (23).

While there is certainly much yet to be learned about acid-catalyzed, hydrocarbon reactions in zeolites, it seems clear that the species we have observed in this study are of fundamental importance in reactor environments. Further spectroscopic examination of these species should do much to · elucidate the hydrocarbon chemistry occurring in zeolites.

SUMMARY

The adsorbed oligomers formed by the adsorption of propene, ethene, and 2-methyl-2-propanol in H–ZSM-5 undergo extensive cracking upon heating to 430 K and desorb as a wide range of olefin products between C_2 and C_7. Examination of the butene isomers in these products indicates that the products formed are in approximately equilibrium proportions. The similarity between these results and those obtained for olefin oligomerization in reactor environments suggests that the chemistry in actual reaction environments is frequently dominated by oligomeric chains of the type observed in this study.

ACKNOWLEDGMENT

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