JOURNAL OF CATALYSIS **154**, 208–215 (1995)

The Role of Propanal in the Reaction of 2-Propen-1-ol in H-ZSM-5

A. I. Biaglow,*[,1] J. Šepa,* R. J. Gorte,*[,2] and David White†

*Department of Chemical Engineering and †Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19104

Received October 27, 1994; revised February 22, 1995

The adsorption of 2-propen-1-ol and propanal has been studied in H-ZSM-5 using simultaneous temperature programmed desorption (TPD) and thermogravimetric analysis (TGA) measurements and ^{13}C NMR. For both adsorbates, the TPD–TGA results are shown to be a strong function of the initial exposure. Following a saturation exposure of either adsorbate, TPD–TGA results for both molecules form a large number of complex products. However, for low exposures, less than one molecule/Brønsted site, the initial products can be observed. For 2-propen-1-ol, the initial reaction product, formed between 400 and 425 K, is propanal, formed through either a secondary cation or an epoxide intermediate. The intact desorption of propanal at low coverages was also observed in this temperature range. ^{13}C NMR spectra of 2-propen-1-ol confirm the formation of propanal and condensation products of propanal. Finally, a potential energy model based on gas-phase proton affinities of the various conjugate bases along possible reaction coordinates for the reaction of 2-propen-1-ol explain the observed chemistry well. © 1995 Academic Press, Inc.

INTRODUCTION

2-Propen-1-ol is an interesting probe molecule for examining acid-catalyzed reactions in zeolites. Besides the fact that dehydration should lead to the relatively stable allylic carbenium ion, this molecule has a second functional group, the carbon–carbon double bond, which can potentially interact with the acid sites and lead to other reaction products. Furthermore, desorption and reaction studies of 2-propen-1-ol have shown that a large number of complex products, including aromatics, aldehydes, and ketones, can be formed from this molecule (1, 2). Therefore, a better understanding of its chemistry is interesting and important.

Recent studies of 2-propen-1-ol in H-ZSM-5 have proven to be controversial. One of the difficulties in understanding the adsorption of 2-propen-1-ol is the apparent sensitivity of the results to the preparation conditions. In an early temperature-programmed desorption (TPD)–thermogravimetric analysis (TGA) study in our laboratory, the results were found to be different, in subtle ways, depending on which of three H-ZSM-5 samples were examined (1). In a reaction study, Hutchings *et al.* reported a change with time on stream from a predominant selectivity to hydrocarbons to selectivity to propanal and acetone (2). Finally, a comparison of the results from two ^{13}C NMR studies of 2-propen-1-ol demonstrates a strong coverage dependence on the species observed (3, 4). In our study, following exposure of the zeolite to less than one molecule per Brønsted site, we observed that the initial species formed by the reaction of 1-^{13}C-2-propen-1-ol exhibited a broad peak at 218 ppm from TMS, which we reported was evidence either for a stable allyl cation or for an unstable secondary cation intermediate that leads to a carbonyl compound with a similar chemical shift. The peak at 218 ppm is consistent with the observations of an allylic carbenium ion in solutions (5–8) but could also be consistent with protonated propanal, which would be formed through the secondary cation as a result of protonation of the C=C double bond, as shown in Scheme 1 of Ref. (3).

In a very recent note, Farcasiu argued against the assignment of the peak at 218 ppm to an allylic cation, basing his argument on three points, which we feel are not only speculative but inconclusive (9). First, contrary to Farcasiu's assertions, we do not observe ether formation or carbon scrambling prior to observing the 218 ppm feature. Allyl ether may be the first product observed at higher adsorbate coverages (4), but not under the conditions of our experiment. The second argument, that allylic cations are not observed above 253 K in solution, may not be applicable to zeolites. The fact that the allyl cation is not observed in solution above 253 K has very little to do with its intrinsic stability. Thermodynamically, it can be shown to be stable in media where protonation occurs. Its disappearance at higher temperatures in solution is primarily due to migration that results in dimerization and polymerization. It is entirely possible that the rigid zeolite lattice, at the low coverages in our study, would tend to minimize this migration. Farcasiu's third argument relates to acidity of the catalyst estimated from H/D exchange

---

[1] Present address: Department of Chemistry, West Point Military Academy, West Point, NY 10996.

[2] To whom correspondence should be addressed.

0021-9517/95 $12.00

studies, from the data of Farneth *et al.* (10). However, these results cannot be used to place H-ZSM-5 on any acidity scale. It is clear from the data in that paper that rapid equilibration occurs between toluene adsorbed at the Brønsted site and physisorbed toluene, leading to a statistical distribution of deuterated toluene at *ortho* and *para* positions, not one limited by kinetic isotope effects.

Obviously, which initial product is formed in the reaction of 2-propen-1-ol and the nature of the species responsible for the 218-ppm peak in the ^{13}C NMR spectrum are important factors. It is evident from our earlier ^{13}C NMR studies that the assignment is ambiguous. Under conditions of higher resolution, namely MAS (Magic Angle Spinning) (3), we have already demonstrated that the spectrum contains several features, ranging from 205 to 218 ppm, suggesting several possibilities that are described in Ref. (3). Nevertheless, we have examined the adsorption of 2-propen-1-ol and propanal, at high and low ($<$1/site) exposures, using TPD–TGA measurements and ^{13}C NMR. The results suggest that most of the unimolecular reaction chemistry of 2-propen-1-ol in H-ZSM-5 can be ascribed to a propanal intermediate, undergoing aldol condensation reactions. The second pathway, involving an allylic carbenium ion, appears to be important only at higher adsorbate concentrations. These results may help explain the changing selectivity observed in the reaction studies of Hutchings *et al.* (2).

EXPERIMENTAL

The TPD–TGA equipment has been described elsewhere (1). Briefly, it consisted of a Cahn microbalance mounted inside a vacuum chamber which had a typical base pressure of 1×10^{-7} Torr. A mass spectrometer, mounted directly in the vacuum chamber, could be used to analyze the composition of products desorbing from the sample. A typical experiment involved heating the zeolite sample in vacuum to 750 K before exposing it to the vapor of the desired adsorbate at room temperature. The adsorbate dose could be controlled by monitoring the sample mass during exposure. Following 1 h evacuation, the sample temperature was ramped at 20 K/min while the sample mass and selected peaks in the mass spectrum were measured.

Two zeolite samples were used in this study. TPD–TGA results for both were similar, showing the same desorption features, products, and trends; however, only the data from H-ZSM-5(B) will be discussed in detail. H-ZSM-5(B), which was prepared by Chemie Uetikon AG (Zeocat-Pentasil-PZ-2/564 Na), had a Brønsted site density of 500 μmol/g measured using TPD–TGA of isopropylamine (11), compared to an Al content of 630 μmol/g. The NMR studies were carried out using H-ZSM-5(A), which was synthesized in our laboratory with a Si/Al ratio of 35 (470 μmol/g) and is the same sample used in our earlier study of 2-propen-1-ol (3). The concentration of Brønsted sites, which is less than the framework Al content, was determined to be 370 μmol/g using TPD–TGA of isopropylamine (11).

For NMR measurements, approximately 200 mg of zeolite was degassed and weighed at 700 K in a Cahn microbalance at 10^{-6} Torr. The samples were then transferred to specially designed glass sample tubes and attached to a vacuum manifold where they were again degassed at 700 K to 10^{-6} Torr. The degassed samples were exposed to controlled amounts of adsorbate using a calibrated volume to permit the small volumes of adsorbate to be known to within 2%. The samples were then sealed in the glass sample tubes without exposure to air and inserted into a homebuilt double-resonance static NMR probe for spin counting measurements, which in all cases were in agreement with the measured dosing volumes. After portions of the samples were transferred in an inert atmosphere to O-ring-sealed rotors, magic angle spinning (MAS) spectra were obtained using a Doty probe (DSI-574). Comparison of the *in situ* broad-line spectra at low surface coverages (or higher resolution spectra at high surface coverages) obtained in the Doty probe and the static probe in the absence of MAS indicated that there were no measurable changes when the samples were transferred from the sealed NMR tubes to the Doty rotors.

The ^{13}C NMR spectra were obtained using a field of 3.5 T (37.84 MHz ^{13}C resonance frequency) using a homebuilt spectrometer that has been described previously (12). The lineshapes were determined from the observation of proton-decoupled Hahn echoes and cross-polarization (CP) spectra. The Hahn echo sequence consisted of a series of $90°-\tau-180°-\tau$ pulses in quadrature, with a delay time, τ, of 30 μs, and a repetition time of 10 s, which was sufficiently long to account for spin–lattice relaxation. The contact time in the CP experiments was 2 ms and the repetition time in these measurements was 1 s. The NMR spectra were acquired at room temperature, with a dwell time of 5 msec and 25 Hz of Lorentzian line broadening added prior to the Fourier transformation of the data. MAS experiments were conducted at various spinning frequencies up to 4.5 kHz.

RESULTS

TPD–TGA Measurements

TPD–TGA curves for 2-propen-1-ol from H-ZSM-5(B) following high and low initial exposures are shown in Figs. 1 and 2. Figure 1, which was obtained after briefly saturating H-ZSM-5(B) with 10 Torr 2-propen-1-ol vapor, followed by evacuation for 2 h, is essentially identical to TPD–TGA curves published previously (1). Starting from

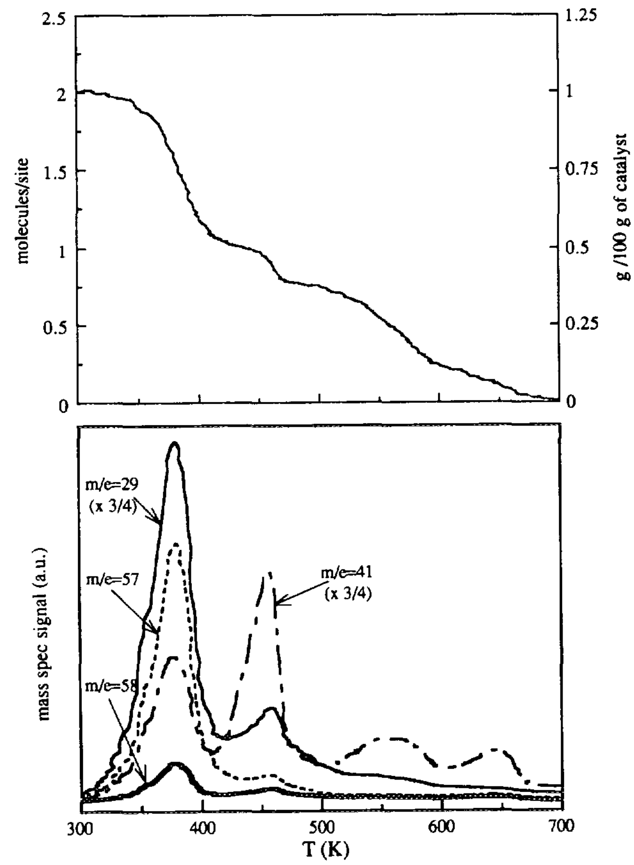


FIG. 1. TPD–TGA curves for 2-propen-1-ol in H-ZSM-5(B), following a saturation exposure.

a coverage of approximately 2 molecule/site, most of the excess 2-propen-1-ol (*m*/*e* = 29, 57, 41, and 58) desorbs from the sample below 400 K, leaving a coverage slightly above 1 molecule per site. (The fragmentation pattern of the desorbing product agrees very well with that obtained from pure 2-propen-1-ol under the conditions of our measurements.) Between 400 and 450 K, some water (not shown) desorbs from the sample, although, as in the previous study (1), the weight change in this temperature region is not sufficient to account for all of the water that would be formed if complete dehydration of the remaining alcohol were to occur. Also, beginning at ~425 K, a number of desorption peaks are observed using the feature at *m*/*e* = 41. While this feature in the mass spectrum can be indicative of many olefins and other hydrocarbon products, previous measurements have shown that the desorption feature between 430 and 475 K is due mainly to propene, a bimolecular product, while the products formed at higher temperatures include a range of olefins and aromatics (1). Even after heating to 750 K, some residue remained in the sample.

Figure 2, which shows the TPD–TGA curves starting from low coverage for 2-propen-1-ol on H-ZSM-5(B), was obtained by exposing the zeolite to a controlled amount of the alcohol (<1 molecule/Brønsted site). The desorption products and features are now very different from those in Fig. 1. First, while none of the 2-propen-1-ol dosed onto the sample could be removed by evacuation at room temperature, some unreacted 2-propen-1-ol again leaves the sample at a temperature below 400 K, as shown by the fragmentation pattern in the mass spectrum, particularly the ratio of peaks at *m*/*e* = 57 and 58. The next desorption product, between 400 and 475 K, is propanal. (The relative intensities of the peaks at *m*/*e* = 57 and 58 are reversed for 2-propen-1-ol and propanal.) Confirmation of this assignment came from a complete analysis of the mass spectrum between *m*/*e* = 10 and 60 at ~425 K, which agreed well with the fragmentation pattern of propanal. At slightly higher temperatures, ~460 K, we start to observe a second hydrocarbon reaction product at *m*/*e* = 41, which may be propene. While the *m*/*e* = 41 peak appears to overlap the peaks at *m*/*e* = 58 and 29 near 450 K in Fig. 2, it is shifted to higher temperatures, implying an additional chemical process. Finally, a range of hydrocarbon products, including aromatics (*m*/*e* = 51, not shown)

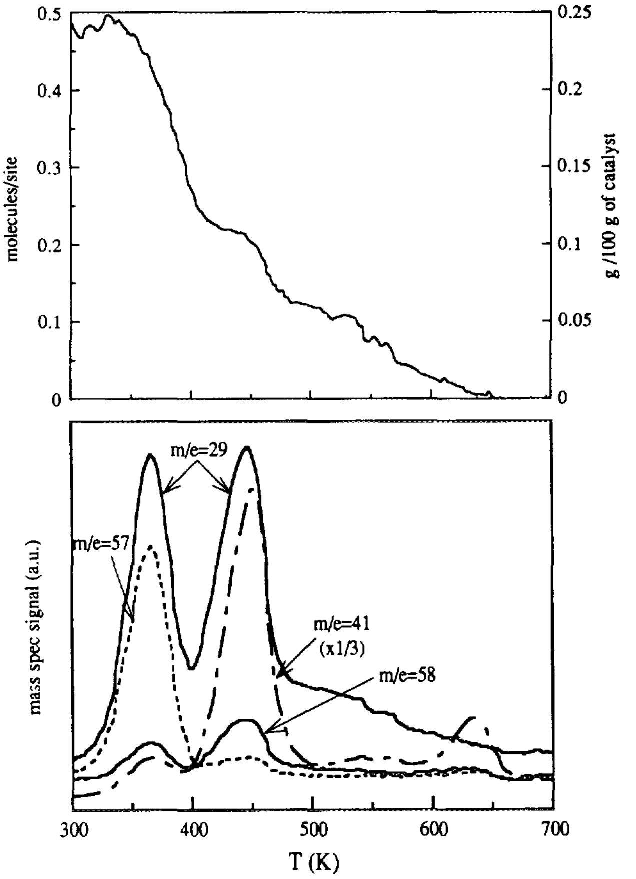


FIG. 2. TPD–TGA curves for 2-propen-1-ol in H-ZSM-5(B), following a low (<1 molecule/site) initial exposure.

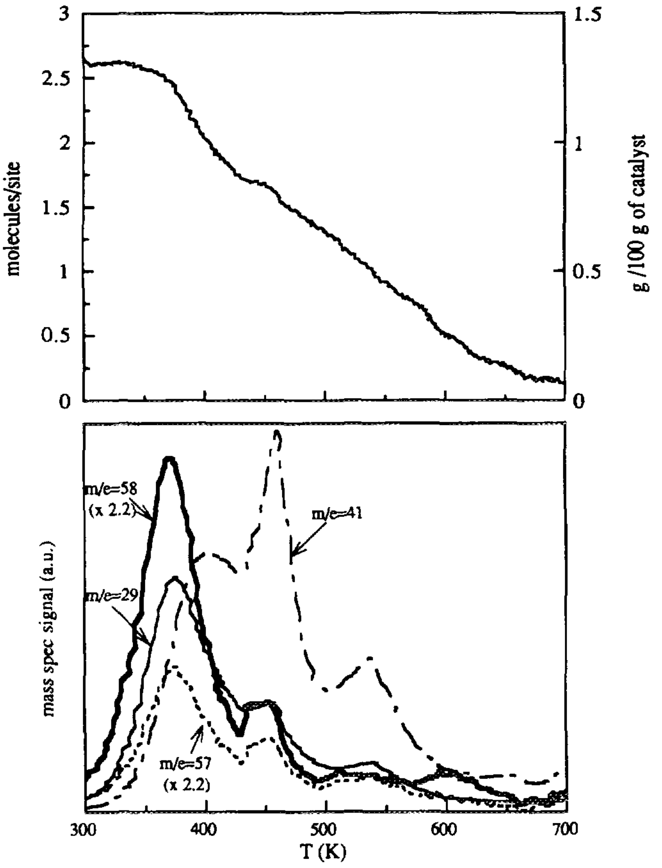


FIG. 3. TPD–TGA curves for propanal in H-ZSM-5(B), following a saturation exposure.

and other olefins (*m/e* = 41), are formed by bimolecular reactions at higher temperatures.

Since propanal is the first product formed during the reaction of 2-propen-1-ol in H-ZSM-5, it is informative to examine the products obtained by adsorption of propanal. Figure 3 is the result obtained following a saturation exposure of propanal on H-ZSM-5(B). Even after evacuation for 2 h, the coverage remained greater than 2.5 molecule/site. The desorption products, too, include a complex mixture. There appears to be some propanal leaving the sample below 400 K; however, the observation, beginning at ∼350 K, of a peak at *m/e* = 41, which is not a major peak in the mass spectrum of propanal, indicates that other products are also present, even at relatively low temperatures. While it was not possible to use the mass spectrum to identify all of the chemical processes which have occurred in the zeolite above 400 K, the products appear to be similar to those observed following 2-propen-1-ol desorption.

Figure 4 is the TPD–TGA curve obtained following a small dose (less than one molecule per Brønsted site) of propanal on H-ZSM-5(B). Below ∼450 K, only unreacted propanal desorbs from the zeolite. A sharp peak at 450 K, also observed in Fig. 3, may be due to the condensation product, 2-methyl-2-propenal, which would be expected to exhibit similar peaks in the mass spectrum. Based on the TGA, the amount of propanal which desorbs at the lower temperatures is relatively small, <0.3 molecule/site. More than half of the propanal desorbs above 450 K as a complex mixture of hydrocarbon products.

^{13}*C NMR*

Taking into account the present TPD–TGA experiments, the ^{13}C NMR spectra published previously for 2-propen-1-ol can now be interpreted unambiguously. The spectrum in Fig. 5a is the proton-decoupled CPMAS spectrum of 1-^{13}C-2-propen-1-ol in H-ZSM-5(A) at a coverage of 0.85 molecule/site after heating to 325 K for 70 h (3). (As discussed elsewhere, a calibration error resulted in all of the spectra of Ref. (3) being offset by 2 ppm (13)). The peak at 69 ppm is unreacted alcohol, hydrogen-bonded to the acid site, while a shoulder at ∼75 ppm corresponds to diallyl ether. The feature at 123 ppm is probably caused by 1–3 label exchange of the carbon in the allylic group

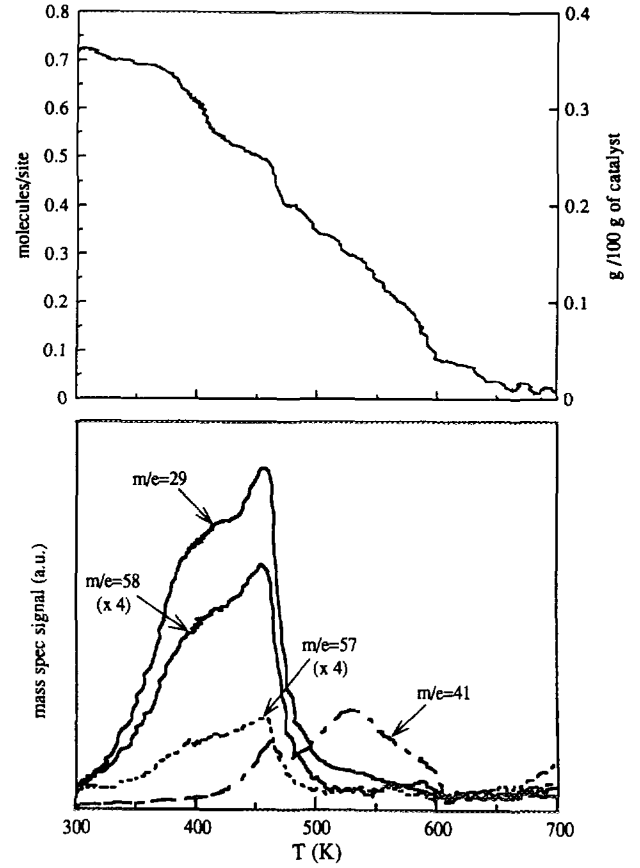


FIG. 4. TPD–TGA curves for propanal in H-ZSM-5(B), following a low (<1 molecule/site) exposure.

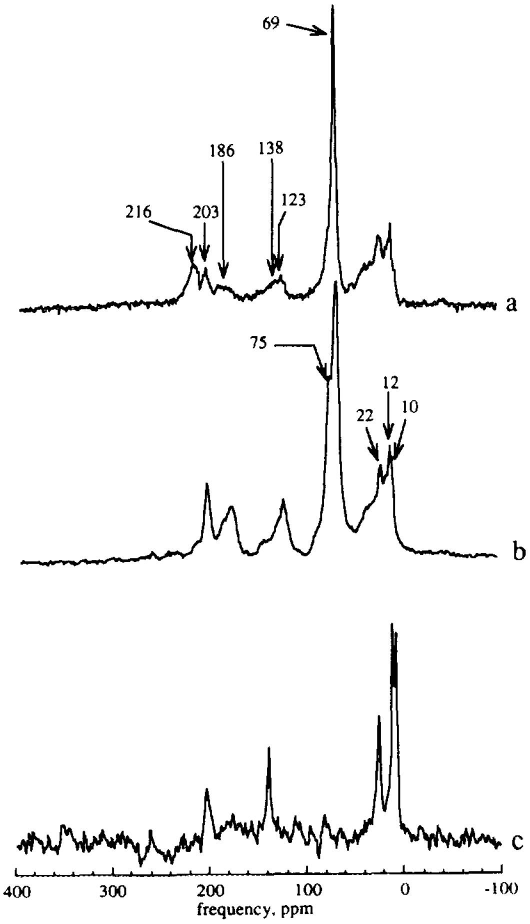
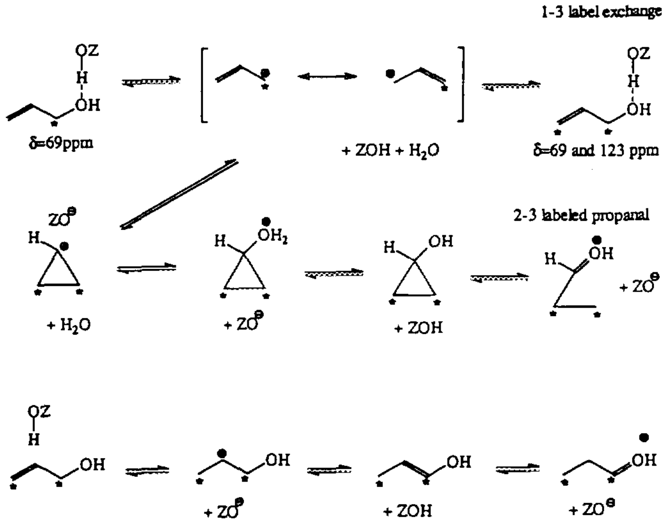


FIG. 5. (a) ^{13}C NMR CPMAS (2.1 kHz) spectrum of 1-^{13}C-2-propen-1-ol adsorbed on H-ZSM-5(A) at a coverage of 0.85 molecules per Brønsted site. The contact time was 1.2 ms, the number of scans was 524,288 and the repetition rate was 100 ms. The sample had been heated to 325 K for 35 h. as discussed in Ref. 3. (b) Same spectrum as in (a), except that the sample was heated to 355 K for 50 h (c) ^{13}C CPMAS spectrum of natural abundance propanal at a coverage of 0.85 molecules/site. A total of 85,188 scans were made at a repetition rate of 500 ms.

of either diallyl ether or 2-propen-1-ol, as shown in Scheme 1. The feature at 216 ppm, previously assigned either to the allylic cation or to a secondary cation giving rise to propanal (3), can now be confidently assigned to propanal hydrogen-bonded to the Brønsted-acid sites. While pure propanal exhibits a shift of 200 ppm, a downfield shift of 16 ppm is entirely consistent with observations for acetone and acetaldehyde adsorbed at the acid sites (14). This reaction to form propanal is shown in Scheme 1. Peaks between 10 and 50 ppm are due to saturated alkyls, such as the CH_3 and CH_2 groups from propanal, as assigned previously (3).

The remaining features can be distinguished more easily in Fig. 5b, which shows the same sample seen in Fig. 5a after it has been heated to 355 K for 50 h. Most notable

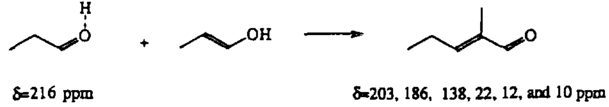


SCHEME 1. Formation of fully labeled propanal.

are the peaks at 203 and 182 ppm and a small shoulder at ~140 ppm. By comparison to similar features observed for mesityl oxide in H-ZSM-5 (14), these features can be assigned to the C-1, C-3, and C-2 positions, respectively, of 2-methyl-2-pentenal, the product formed by aldol condensation of propanal, as shown in Scheme 2. Pure methylpentenal would show features at 195, 156, and 139 for these three carbons; but, as for the C-2 and C-4 carbons of mesityl oxide, the C-1 and C-3 are strongly affected by hydrogen bonding between the carbonyl carbon and the acid site. Additional evidence for the assignment of these three peaks to 2-methyl-2-propenal are shown in Fig. 5c, which is the CPMAS spectrum of unenriched propanal at a coverage of 0.85 molecule/site. Due to the long time and relatively high coverage required for taking the spectrum, we appear to have formed the condensation product. The peaks at 203 and 140 ppm are clearly present, while the 180 ppm feature is broad and more difficult to see, but also observable. In agreement with the TPD–TGA study, the NMR results demonstrate the high reactivity of propanal.

DISCUSSION

The similarities in the adsorption results for 2-propen-1-ol and propanal, and the observation of propanal as the first reaction product from 2-propen-1-ol in TPD, indicate



SCHEME 2. Condensation of propanal.

that the reaction of 2-propen-1-ol in H-ZSM-5 at low adsorbate coverages occurs primarily through a propanal intermediate. At higher coverages, it appears that a bimolecular reaction, through an allyl ether intermediate which should not be able to form the aldehyde, may also be important (4), although similar hydrocarbon products are formed by aldol condensation reactions of the aldehyde. However, the following important questions remain: Are both of these mechanisms important under reaction conditions? Can the reaction environment change the mechanism and, therefore, the reaction selectivity? Is the formation of a propanal intermediate energetically reasonable?

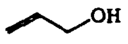
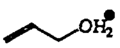
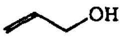
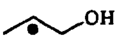
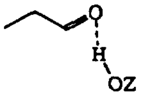
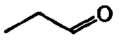
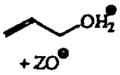
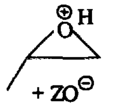
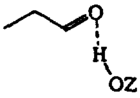
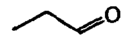
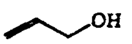
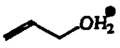
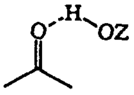
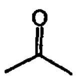
The results of Hutchings *et al.* (2) provide strong evidence that the propanal reaction pathway is important, at least under their conditions. Their observation of a change in selectivity for the reaction of 2-propen-1-ol in H-ZSM-5 with time on stream suggests that the propanal pathway dominates on the coked sample, possibly because the bimolecular reactions, aldol condensations, and formation of diallyl ether are suppressed. Coking will likely reduce the concentration of the reactant 2-propen-1-ol near the Brønsted sites and favor the unimolecular reaction products.

It is interesting to consider the thermodynamic reasonability of forming propanal from 2-propen-1-ol, compared to the formation of the allylic cation using the thermochemical scheme developed previously for describing the reactions of 2-propen-1-ol and other alcohols in H-ZSM-5 (1, 15). This calculation of the reaction coordinate, which assumes that adsorption complexes are formed by complete transfer of the acidic proton from the zeolite and that heats of formation of the adsorption complexes scale with gas-phase proton affinities, did very well at rationalizing the reactivities of the entire series of alcohols and for understanding the relative heats of adsorption for a series of amines in H-ZSM-5 (16).

We assume that the reaction of 2-propen-1-ol occurs through the intermediates shown in Table 1. The heats of formation of adsorption complexes formed along the reaction coordinates are assumed to increase linearly with the gas-phase proton affinities of the conjugate bases, using results for ammonia ($\Delta H_{\text{adsorption}}$ equal to -145 kJ/mol (16, 17)) to anchor the scheme. For example, the gas-phase proton affinities of ammonia (PA = 858 kJ/mol) and 2-propen-1-ol (PA = 791 kJ/mol) differ by 67 kJ/mol. The heat of formation of the adsorption complex for 2-propen-1-ol ($CH_2{=}CH{-}CH_2OH_2^+ \cdots ZO^-$) is therefore estimated to be -78 kJ/mol (-145 kJ/mol + 67 kJ/mol)

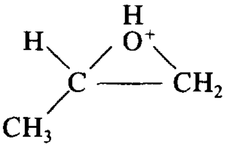
TABLE 1

Calculated Energies in kJ/mol for Competing Reactions[a]

 + ZOH	 + ZO$^{\ominus}$	 + ZO$^{\ominus}$	$H_2C{=}C{=}CH_2$ + ZOH + H_2O	
0	-78	+4.2	+73	
 + ZOH	 + ZO$^{\ominus}$		 + ZOH	
0	(-55)	-149	-61	
 + ZOH	 + ZO$^{\ominus}$	 + ZO$^{\ominus}$		 + ZOH
0	-78	(-70)	-149	-61
 + ZOH	 + ZO$^{\ominus}$			 + ZOH
0	-78		-210	-93

[a] Values in parentheses were determined from *ab initio* calculations, optimized at Hartree-Fock/6-31G* level.

relative to the unadsorbed alcohol. The adsorption complex formed by propanal (PA = 801 kJ/mol) can be scaled to the unadsorbed 2-propen-1-ol in the same way using the standard heat of reaction (−61 kJ/mol) added to the calculated heat of adsorption for propanal ($-145 + (858 - 801) = -88$ kJ/mol) to give a value of −149 kJ/mol. The formation of propanal can occur through either a secondary cation formed by proton transfer to the C=C double bond, $CH_3\text{-}CH^+\text{-}CH_2OH \cdots ZO^-$, or through an epoxide:



Based on *ab initio* calculation, it appears that the epoxide is the slightly more stable intermediate.

Other assumptions in the model have been discussed in detail elsewhere (15, 16). Obviously, only the interactions with the acidic hydroxyl are included and dispersion forces are not accounted for. The model also assumes complete proton transfer, while the actual bonding between the zeolite and the adsorbate is best described as a hydrogen bond (13, 14). However, the assumption of complete proton transfer does appear to provide a good starting point for describing the chemistry and may provide a reasonable estimate of the heat of adsorption for the complex because the strength of hydrogen bonds is known to scale with proton affinities (18). In agreement with this, the measured heats of adsorption for acetone at coverages below 1 molecule/site were found to be between 100 and 120 kJ/mol (19), while the calculated heat of adsorption was 114 kJ/mol.

If one assumes that there are no large energy barriers separating the various complexes shown in Table 1, the energies listed in the table allow one to predict which reactions should occur most easily. For example, while it is clear that protonation of the 2-propen-1-ol to form the oxonium ion $CH_2\text{=}CH\text{-}CHOH_2^+ \cdots ZO^-$, is preferred over formation of the secondary cation $CH_3\text{-}CH^+\text{-}CH_2OH \cdots ZO^-$, the difference between these species should be small, only ~23 kJ/mol. The energy difference between the oxonium ion and the epoxide is predicted to be even smaller, ~8 kJ/mol. In contrast, the barrier to formation of the allylic carbenium ion from the oxonium ion is ~80 kJ/mol. Since it is only necessary for the secondary cation to undergo a hydride shift to arrive at propanal, an intermediate which is energetically downhill from the oxonium ion, or for ring opening to occur in the epoxide, reaction to the aldehyde is favored over dehydration. Reaction to acetone would also appear to be favored; however, formation of acetone either by ring opening of the epoxide or by reaction of the secondary cation would require formation of a primary carbocation, which would be energetically unfavored (21).

It is interesting to compare the reactivity of propanal to that of acetone and acetaldehyde, both of which have been examined recently in our laboratory (14). In the case of both acetone and acetaldehyde, the mobility of the adsorbed complex appears to play a major role in the reactivity. The mobility of acetone in H-ZSM-5, based on the changes in the ^{13}C NMR powder-averaged lineshapes of the chemical shift tensor, showed a dramatic increase for the molecules adsorbed an acid sites at room temperature when surface coverage was increased above 1 molecule/site (20). The onset of mobility also lead to the formation of condensation products at room temperature (14). Mobility, and the onset of condensation reactions, can be induced thermally at coverages below 1 molecule/Al; however, temperatures in excess of 400 K are necessary for this to occur.

It is evident from both ^{13}C NMR and TPD–TGA studies that acetaldehyde and propanal undergo aldol condensation much more readily under similar surface coverages and temperatures than does acetone. This could be due to either increased translational and rotational mobility at the Brønsted site, or a change in the lifetime of the enol form by transient proton transfer (caused by a concerted process involving framework dynamics together with collisions), or both. A detailed picture of localized dynamics at a Brønsted site is as yet not available, although it clearly must arise from the coupling width and dynamics of the framework. It should be possible to gain further insight into this dynamics using simulations when models closely replicating the physical situation can be used in conjunction with large computations.

SUMMARY

Simultaneous TPD–TGA measurements of 2-propen-1-ol and propanal in H-ZSM-5 indicate that the first product formed by the reaction of 2-propen-1-ol at low coverages is propanal, which results either from protonation of the carbon–carbon double bond to form a transient secondary cation or from an epoxide species. Based on ^{13}C NMR measurements, aldol condensation reactions of the propanal formed in the initial stages of the reaction can account for many of the other products formed from 2-propen-1-ol as well. Finally, a simple model for calculating the energies of adsorbed species along the reaction coordinates for possible reactions of 2-propen-1-ol, based on the gas-phase proton affinities of the conjugate bases, demonstrates the reasonability of forming the secondary cation in preference to the allylic cation.

ACKNOWLEDGMENTS

This work was supported by NSF Grant CTS94-03909. We also thank E. Evleth for calculating the energies of two possible intermediates in the reaction of 2-propen-1-ol.

Note added in proof. We acknowledge the recent publication by T. Xu, J. H. Zhang, E. J. Munson, and J. F. Haw, *J. Chem. Soc. Chem. Comm.*, 2733, (1994), which appeared during the review process of the above manuscript. This publication repeats the earlier NMR studies of Munson, Xu, and Haw, Ref. (4), but under the experimental conditions reported in our earlier ^{13}C NMR studies, Ref. (3). With the exception of a calibration error in Reference (3), which we have corrected here and in Ref. (14), we are pleased to note that their experimental NMR results are nearly identical to ours and demonstrate very clearly the importance of working at low surface coverages (less than one adsorbed molecule per Brønsted-acid site) when identifying the initial surface complexes as well as the primary reaction processes. This, we should note, has been characteristic of all of our studies. (For example, see Ref. (14).)

REFERENCES

1. Pereira, C., Kokotailo, G. T., Gorte, R. J., and Farneth, W. E., *J. Phys. Chem.* **90,** 2063 (1990).
2. Hutchings, G. I., Lee, D. F., and Williams, C. D., *J. Chem. Soc. Chem. Commun.*, 1475 (1990).
3. Biaglow, A. I., Gorte, R. J., and White, David, *J. Chem. Soc. Chem. Commun.*, 1164 (1993).
4. Munson, E. J., Xu, T., and Haw, J. F., *J. Chem. Soc. Chem. Commun.*, 75 (1993).
5. Olah, G. A., and Spear, R. J., *J. Am. Chem. Soc.* **97,** 1539 (1975).
6. Olah, G. A., Clifford, P. R., Halpern, Y., and Johanson, R. G., *J. Am. Chem. Soc.* **93,** 4319 (1971).
7. Olah, G. A., Comisarow, M. B., *J. Am. Chem. Soc.* **86,** 5682 (1964).
8. Olah, G. A., and Mayr, H., *J. Am. Chem. Soc.* **98,** 7333 (1976).
9. Farcasiu, D., *J. Chem. Soc. Chem. Commun.*, 1801 (1994).
10. Farneth, W. E., Roe, D. C., Kofke, T. J. G., Tabak, C. J., and Gorte, R. J., *Langmuir* **4,** 152 (1988).
11. Kofke, T. J. G., Gorte, R. J., and Farneth, W. E., *J. Catal.* **114,** 34 (1988).
12. Carduner, K. R., Villa, M., and White, D., *Rev. Sci. Instrum.* **55,** 68 (1984).
13. Biaglow, A. I., Gorte, R. J., Kokotailo, G. T., and White, D., *J. Catal.* **148,** 779 (1994).
14. Biaglow, A. I., Sepa, J., Gorte, R. J., and White, D. *J. Catal.* **151,** 373 (1995).
15. Aronson, M. T., Gorte, R. J., and Farneth, W. E., *J. Catal.* **98,** 434 (1986).
16. Parrillo, D. J., Gorte, R. J., and Farneth, W. E., *J. Am. Chem. Soc.* **115,** 12441 (1993).
17. Parrillo, D. J., Lee, C., and Gorte, R. J., *Appl. Catal. A* **110,** 67 (1994).
18. Meot-Ner, M., *J. Phys. Chem.* **91,** 417 (1987).
19. Lee, C.-C., and Gorte, R. J., unpublished data.
20. Biaglow, A. I., Gorte, R. J., and White, D., *J. Phys. Chem.* **97,** 7135 (1993).
21. Morrison, R. T., and Boyd, R. N., "Organic Chemistry," 3rd Ed., p. 569. Allyn & Bacon, Needham Heights, MA, 1973.