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An Infrared Spectroscopy Study of Simple Alcohols Adsorbed on H-ZSM-5

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We have examined the adsorption of methanol, ethanol, 1-propanol, 1-butanol, 2-propanol, and 2-methyl-2-propanol on H-ZSM-5 using transmission infrared spectroscopy. In agreement with previous results from temperature-programmed desorption (TPD) and thermogravimetric analysis [M. T. Aronson, R. J. Gorte, and W. E. Farneth, *J. Catal.* **98,** 434 (1986)], each of the alcohols adsorbs in the vicinity of the Al atoms, as evidenced by the disappearance of the hydroxyl band associated with the hydrogen cation. For 2-methyl-2-propanol adsorbed at 295 K and 2-propanol at 360 K, changes in the IR spectral features and isotopic scrambling following exposure to D_2O indicate that these molecules dehydrate to form carbenium ion-like intermediates prior to desorbing as olefin products. Methanol, ethanol, and 1-propanol remain unreacted up to their desorption temperatures. While 1-butanol is shown to be very reactive in TPD, no isotopic scrambling was observed during exposure to D_2O and reaction appears to occur through a bimolecular mechanism. The results of this study are explained in terms of a model which assumes that the primary interaction between the alcohols and the zeolite is due to proton transfer at the Al sites. The model pictures the adsorbed species as ion pairs consisting of oxonium ions or carbenium ions coupled with the anionic zeolite framework.

INTRODUCTION

We recently examined the adsorption of a series of simple alcohols on H-ZSM-5 using temperature-programmed desorption (TPD) and thermogravimetric analysis (TGA) to investigate the acid sites in this zeolite (*1*). For each of the alcohols except 1-butanol, we found that there exists a clearly defined desorption state corresponding to one molecule per Al atom in the zeolite and that the reactivity of this molecule is different for primary, secondary, and tertiary alcohols. For the tertiary and secondary alcohols, 2-methyl-2-propanol and 2-propanol, this molecule at the Al site completely reacts and desorbs as olefinic products and water. For methanol and the primary alcohols, ethanol and 1-propanol, the majority of the adsorbed molecules at the Al sites desorb unreacted.

The results of this study were explained in terms of a model which assumes that the primary interaction between the alcohols and the zeolite is due to proton transfer at the Al sites. The model pictures the adsorbed species as ion pairs consisting of oxonium ions or carbenium ions coupled with the anionic zeolite framework. Accordingly, differences in the reactivities of various alcohols are due to the relative energetic accessibilities of the intermediate carbenium ions that must form for reaction to occur. Therefore, 2-propanol and 2-methyl-2-propanol are much more reactive than the primary alcohols because of the increased stability of the secondary and tertiary carbenium ions that they can form.

In this paper, we present an IR spectroscopic study complementary to our previous TPD/TGA work on alcohol structure variation on H-ZSM-5. Previous work has already shown that the adsorbed secondary alcohol, 2-propanol, undergoes irreversible spectral changes when heated to temperatures lower than that needed for desorption

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(*2*). We show here that the main spectral features for the primary alcohols remain unchanged, even at high temperatures, while 2-methyl-2-propanol dehydrates at room temperature. Both the reacted 2-propanol and 2-methyl-2-propanol exhibit interesting isotope-exchange properties upon exposure to D_2O, consistent with the presence of carbenium ions at low temperatures.

EXPERIMENTAL TECHNIQUES

The infrared cell used for these experiments has been described previously, (*3*). A self-supporting, 35-mg wafer, 1.6 cm in diameter, was placed in a gold-plated copper tube which could be heated to 800 K using a cartridge heater. The sample temperature was measured with an iron–constantan thermocouple attached to the tube supporting the sample. The sample could be evacuated with a liquid-nitrogen-trapped mechanical pump. TPD and IR results showed that the sample could be kept clean for several hours in this system.

In each case, the alcohols were adsorbed by exposing the sample to the equilibrium vapor pressure above a liquid at 295 K. Exposure times were approximately 30 s since adsorption was fast and longer exposure times gave identical results. Following exposure, samples were reevacuated under conditions that had been shown to lead to the 1 : 1 stoichiometry in previous TGA experiments (*1*). For example, the spectrum in Fig. 2a was generated by exposure at 295 K, followed by evacuation for 1 h. Those spectra reported at higher temperatures were measured after adsorption at 295 K, evacuation, heating of the sample to the indicated temperature *in vacuo*, and cooling to 295 K. For experiments in which adsorbed alcohols were exposed to H_2O or D_2O, the H_2O or D_2O was adsorbed briefly five times at the indicated temperature, with evacuation between exposures. Adsorption and sample heating were always performed out of the IR beam to minimize additional radiative heating.

The zeolite samples were obtained as an NH_4-ZSM-5 powder from the Mobil Oil Company. Electron microscopy indicated that the zeolite particles were uniformly between 0.4 and 0.5 μm in diameter. X-ray diffraction of these samples agreed with the published data for ZSM-5 (*4*). We checked the silica–alumina ratio by measuring the desorption of NH_3 from NH_4-ZSM-5 and obtained a ratio of 72, in good agreement with the value of 70 reported to us by Mobil. All experiments reported in this paper were performed on H-ZSM-5 prepared by heating NH_4-ZSM-5 to 700 K *in vacuo*. D-ZSM-5 was prepared by exposing H-ZSM-5 to D_2O, followed by heating to 500 K *in vacuo* to ensure that excess D_2O had been removed.

All IR spectra were obtained using a Nicolet Model 4250 grating-type spectrophotometer and were measured between 1300 and 3900 cm^{-1}. Poor transmission below 1300 cm^{-1} prevented our examining vibrational modes in the low-frequency region. Since we did not observe any features attributable to adsorption between 1600 and 2000 cm^{-1}, the spectra in this paper are only shown between 1300 and 1600 cm^{-1} and between 2000 and 3900 cm^{-1} for simplicity.

The IR spectra corresponding to clean H-ZSM-5 and D-ZSM-5 are given in Fig. 1. Clean H-ZSM-5 is characterized by two hydroxyl peaks at 3740 and 3605 cm^{-1} which have been identified as being due to silanol groups present at the edges of the zeolite crystals and to the hydrogen cations associated with the Al atoms in the zeolite respectively (*5–7*). In addition, the broad underlying feature between 3300 and 3700 cm^{-1} has recently been assigned to internal silanol groups which are nonacidic (*8*). Clean D-ZSM-5 is characterized by the analogous O–D peaks at 2755 and 2655 cm^{-1}.

RESULTS

The spectral features observed for the adsorbed alcohols are reported in Table 1, along with the features for the pure gas-phase alcohols. The IR spectra of the ad-

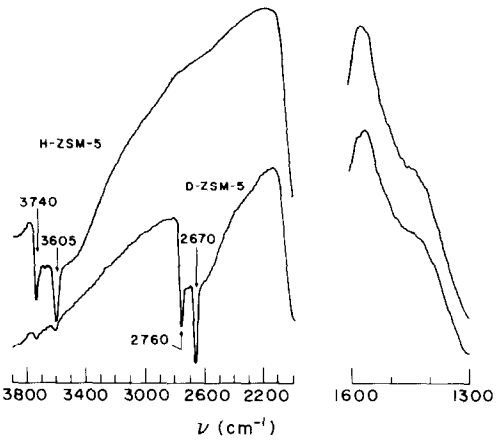


FIG. 1. IR spectra corresponding to clean H-ZSM-5 and D-ZSM-5. Clean H-ZSM-5 is characterized by two hydroxyl peaks at 3740 and 3605 cm^{-1} which have been identified as being due to silanol groups present at the edges of the zeolite crystals and to hydroxyl groups associated with the Al atoms in the zeolite, respectively. Clean D-ZSM-5 is characterized by the analogous O–D peaks at 2760 and 2670 cm^{-1}.

sorbed alcohols in the 1 : 1 stoichiometry share some common features. In each case, the zeolite peak at 3740 cm^{-1} remains unchanged following evacuation, indicating that no adsorption is localized at the external silanol groups. The peak at 3605 cm^{-1}, however, is replaced in all the spectra by a broad band centered at approximately 3500 cm^{-1}, implying that the protons associated with the Al atoms are coupled with the adsorbed alcohols. We discuss the additional results specific for each alcohol individually.

2-Methyl-2-propanol

Our previous work has shown that 2-methyl-2-propanol decomposes on H-ZSM-5 on chemisorption at 295 K (*1*). Most of the water formed during dehydration can be removed from the sample by evacuation at

TABLE 1[a]

	ν(C–H)	δ(C–H)	δ(C–OH)	ν(C–OH)	Unknown[b]
2-Methyl-2-propanol					
Gaseous	3000–2800	1460, 1390–1360	1320	1150–1140	
As adsorbed, 295 K	2960, 2940, 2880	1465, 1455, 1370	—	—	
2-Propanol					
Gaseous	3000–2800	1460, 1390–1360	1240	1120–1100	
As adsorbed, 295 K	2980, 2940, 2880	1465, 1455, 1380, 1360	—	—	
Heated to 360 K	2960, 2940, 2880	1465, 1455	—	—	
Methanol					
Gaseous	3000–2800	1460, 1380	1320	1050	
As adsorbed, 295 K	2960, 2860	1455	—	—	
Ethanol					
Gaseous	3000–2800	1460–1450, 1380–1375	1230	1075–1010	
As adsorbed, 295 K	2980, 2940, 2920	1450, 1390	—	—	1500 (—)
1-Propanol					
Gaseous	3000–2800	1460–1450, 1380–1375	1215	1075–1010	
As adsorbed, 295 K	2980, 2940, 2880	1455, 1385	—	—	1435 (1435)
Heated to 375 K	2980, 2940, 2880	1455, 1385	—	—	1560 (1560) 1435 (1435)
Heated to 450 K	2980, 2940, 2880	1455	—	—	1510 (1470)
1-Butanol					
Gaseous	3000–2800	1460–1450, 1380–1375	1200	1075–1010	
As adsorbed, 295 K	2980, 2940, 2880	1465, 1455, 1385	—	—	1500 (—) 1435 (1435)
Heated to 375 K	2980, 2940, 2880	1465, 1455, 1385	—	—	1500 (—) 1435 (1435)
Heated to 475 K	2980, 2940, 2880	1465, 1455	—	—	1510 (1470

[a] All gaseous data taken from A. V. Stuart and G. B. B. M. Sutherland, *J. Chem. Phys. 24*, 559 (1956).
[b] Frequency in parentheses corresponds to location of unassigned peak following D_2O adsorption.

room temperature prior to beginning a TPD experiment. This high reactivity is corroborated by the infrared results.

Figure 2 shows the IR spectra for 2-methyl-2-propanol on H-ZSM-5 before and after D_2O adsorption at 295 K. Before D_2O adsorption, the spectrum is characterized by at least three peaks in the C–H stretching region at 2960, 2940, and 2880 cm^{-1} and by an asymmetric methyl bend centered at 1460 cm^{-1}. There is also a weak symmetric methyl bend around 1370 cm^{-1}. Since the peak at 3605 cm^{-1} has essentially disappeared and since TGA results indicate that there is one molecule adsorbed per Al atom following evacuation at 295 K, this adsorbed species must be interacting with the Al site in the zeolite (*1*).

The infrared spectra clearly indicate that this adsorbed species at the Al site has already reacted. First, there is only a small peak at 1370 cm^{-1} in Fig. 2a. For the unreacted alcohol, a very intense doublet is observed near this frequency. The intact alcohol mode has been assigned to a *gem*-dimethyl bend. The remaining weak absorbance can be ascribed to a symmetric methyl bend observed in this region whenever a methyl group is present. Second, deuterium from D_2O exchanges into the C–H bonds at 295 K. Following exposure of the adsorbed alcohol to D_2O, the hydroxyl peak at 3740 cm^{-1} and the broad peak centered at 3500 cm^{-1} are replaced by their deuterium analogs at 2755 and 2600 cm^{-1}, respectively, as expected. More interesting, however, are the appearance of peaks in the C–D stretching region at 2220 and 2100 cm^{-1} and the significant changes in the shape and the intensity of bands in the C–H stretching region. Likewise, the peak centered at 1460 cm^{-1} in the C–H bending region has disappeared. This is clear evidence that deuterium is exchanging into the adsorbed species and forming C–D bonds at the expense of C–H bonds, even at these low temperatures. Such exchange would not be expected if the adsorbed alcohol had not reacted. It suggests that the C–H bonds are significantly more polarized in the reacted adsorbate than in the intact adsorbate.

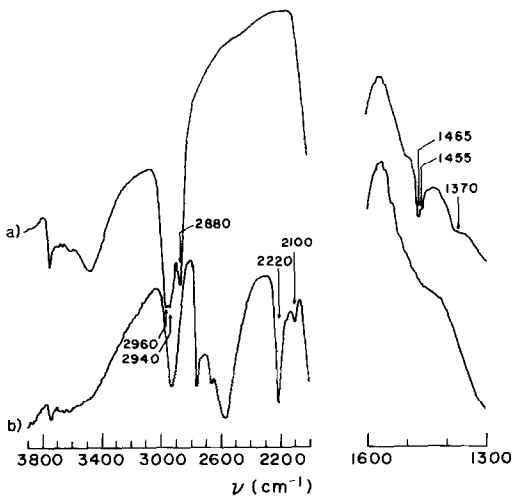


FIG. 2. 2-Methyl-2-propanol adsorbed on H-ZSM-5 before (a) and after (b) exposure to D_2O at 295 K. Exposure to D_2O results in the formation of C–D bonds in the adsorbed alcohol.

There are several additional interesting features to the spectra shown in Fig. 2. First, there are at least three peaks in the C–H stretching region for 2-methyl-2-propanol before D_2O adsorption, whereas there are only two peaks in the C–D stretching region following D_2O adsorption. This could indicate that only a subset of the adsorbed species exchanges, or it could reflect the presence of overtones or combination modes in the C–H region that are not present in the C–D region. To determine the origin of the multiple C–H stretching modes, we examined the adsorption of $(CD_3)_3COD$, with the results shown in Fig. 3. The deuterated alcohol has only two peaks in the C–D stretching region before H_2O adsorption and regenerates the three-peaked C–H spectrum on exposure to H_2O. Therefore, some of the peaks in the C–H stretching region are due apparently to a coupling of stretching modes with bending modes, and the complexity does not reflect multiple adsorbed species. Figures 2 and 3 show that exchange is completely revers-

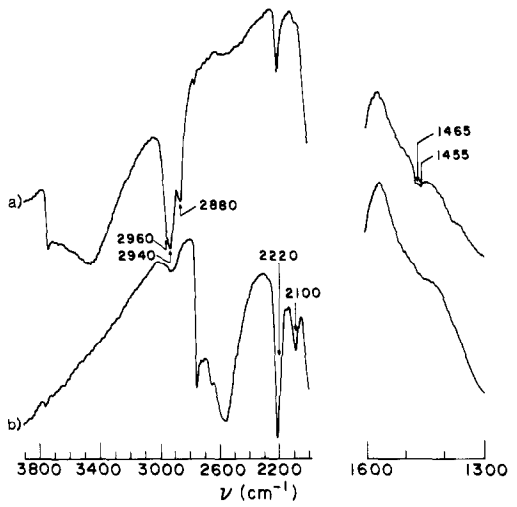


FIG. 3. Deuterated 2-methyl-2-propanol [$(CD_3)_3$ COD] adsorbed on D-ZSM-5 before (b) and after (a) exposure to H_2O at 295 K.

ible and any apparent differences in the intensity of the C–H and C–D stretches are due to differences in the absorbance scale. Second, Fig. 2 shows a broad hydroxyl band around 3500 cm^{-1}. Evidence has recently been presented that ZSM-5 always has internal silanol groups which are nonacidic and are characterized by a broadband at 3500 cm^{-1} (*8*). Therefore, this band is not necessarily part of the adsorbed species.

Because of the absence of characteristic peaks, the spectrum of the adsorbate is not consistent with either an adsorbed alcohol or an olefin. The absence of the expected feature at 1380 cm^{-1} for the gaseous molecule has already been discussed. A C–OH bend is also present in the gaseous alcohol at 1325 cm^{-1} but its position is highly variable and can shift below 1200 cm^{-1} in some solvents (*9*). An olefin should exhibit a $C{=}CH_2$ stretch near 1640 cm^{-1} and C–H stretches above 3000 cm^{-1}. While it is possible that a peak near 1640 cm^{-1} could have been obscured by the broad zeolite band in this region, we should have been able to observe a higher-frequency C–H mode if the adsorbate had an olefinic structure. The vibrational bands we observe are consistent with those reported for t-butyl carbenium ions in FSO_3H–SbF_5–SO_2 (*10*). Raman spectra of these ions exhibited only the following peaks above 1200 cm^{-1}: 2947, 2850, 1450, and 1295 cm^{-1}.

2-Propanol

Figure 4a shows the IR spectrum of 2-propanol on H-ZSM-5 after adsorption at 295 K. The C–H stretches between 3000 and 2800 cm^{-1} and the asymmetric methyl and *gem*-dimethyl bends centered at 1460 and 1370 cm^{-1}, respectively, are characteristic of gaseous 2-propanol. The C–OH bending mode, which is not observed, occurs at 1240 cm^{-1} for gaseous 2-propanol; however, the position of this peak is known to be strongly dependent on changes of state and solvent composition and can shift significantly in hydrogen-bonding environments (*9*). The effect of D_2O adsorption can be seen in Fig. 4b. The O–H groups exchange to O–D groups, but the C–H stretching and bending regions remain unchanged. No new peaks appear in the C–D stretching region.

Heating the sample to 360 K results in several changes in the C–H stretching and bending regions, as can be seen in Fig. 5a. The peaks at 2980, 2940, and 2880 cm^{-1} have been replaced with a new peak at 2960 cm^{-1} and more intense peaks at 2940 and

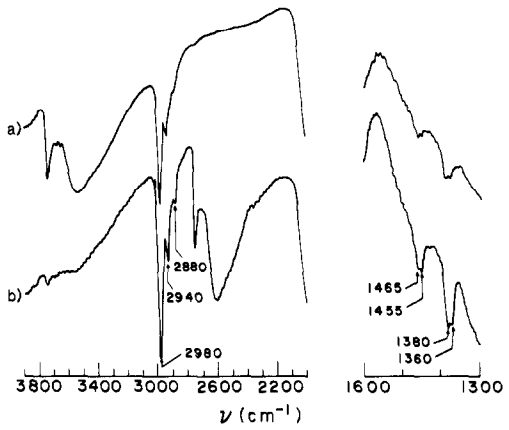


FIG. 4. 2-Propanol on H-ZSM-5 before (a) and after (b) exposure to D_2O at 295 K.

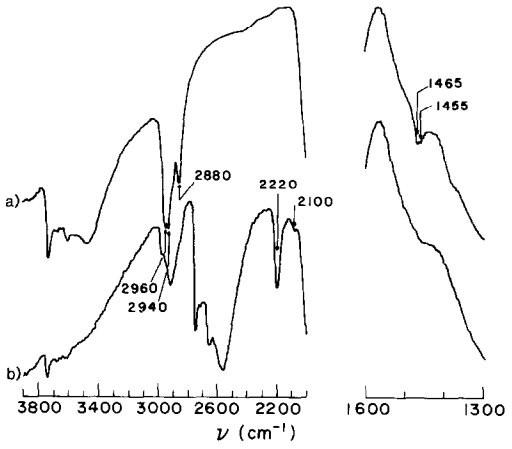


FIG. 5. 2-Propanol on H-ZSM-5 before (a) and after (b) exposure to D_2O following heating to 360 K. Heating to 360 K results in the reaction of the adsorbed alcohol and exposure to D_2O causes the formation of C–D bonds.

2880 cm^{-1}. In the C–H bending region, the peak centered at 1370 cm^{-1} has disappeared, whereas the peak centered at 1460 cm^{-1} remains unchanged. These observations, previously reported by Grady and Gorte (*2*) clearly indicate that the adsorbed species has reacted.

When D_2O is admitted to the cell containing the adsorbed alcohol at 360 K, one again observes the exchange of C–H groups for C–D groups as shown in Fig. 5b. Following D_2O exposure, the peaks in the C–H stretching region decrease while two peaks form in the C–D stretching region at 2220 and 2100 cm^{-1}. The peak centered at 1460 cm^{-1} also disappears. The ability to incorporate deuterium into 2-propanol that has been heated to 360 K, but not into 2-propanol at 295 K, is further evidence that reaction occurs when the adsorbed alcohol is heated to 360 K. Furthermore, the similarity in the spectral changes to those observed with 2-methyl-2-propanol at room temperature suggests that the chemistry is the same.

Figure 6 demonstrates the results for deuterated 2-propanol, $(CD_3)_2CDOD$, on D-ZSM-5. The figure shows the spectra recorded after adsorption at 295 K, after heating to 360 K, and after exposing the heated sample to H_2O. After heating, we observe a shift in the deuterated methyl stretching modes from 2240 and 2130 cm^{-1} to 2220 and 2100 cm^{-1}, again indicating that reaction has occurred. Exposing this species to H_2O at 360 K results in the formation of at least three peaks in the C–H stretching region and almost complete elimination of the peaks in the C–D stretching region, as shown in Fig. 6a. As with 2-methyl-2-propanol, the multiple C–H stretching frequencies are apparently due to coupling between bending and stretching modes. A small asymmetric methyl bend also appears around 1455 cm^{-1}. Again, peaks characteristic of an olefin at 1640 cm^{-1} and above 3000 cm^{-1} were not observed.

While we did not attempt to quantify the rates for deuterium incorporation into the intermediates formed from 2-methyl-2-propanol at 295 K and from 2-propanol that had been heated to 360 K, it was readily apparent that deuterium exchange into the 2-methyl-2-propanol intermediate was much more rapid. The spectral changes

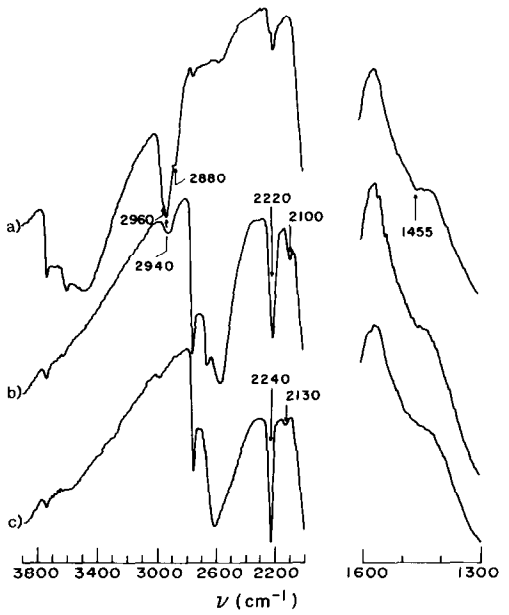


FIG. 6. Deuterated 2-propanol [$(CD_3)_2CDOD$] adsorbed on D-ZSM-5 at 295 K (c), after heating to 360 K (b), and following exposure to H_2O at 360 K (a).

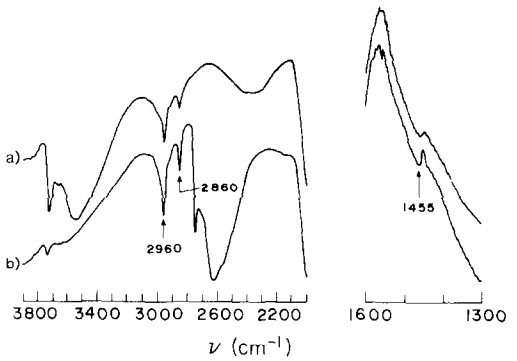


FIG. 7. Methanol adsorbed on H-ZSM-5 before (b) and after (a) exposure to D_2O at 295 K.

which occurred when 2-propanol was heated to 360 K were irreversible, and the spectrum was unchanged by cooling to 295 K. However, when D_2O was exposed to adsorbed 2-propanol that had been heated to 360 K to induce reaction and cooled back to 295 K, the incorporation of deuterium was very slow, in agreement with results reported by Grady and Gorte (*2*). Higher temperatures were needed to obtain significant deuterium exchange rates.

Methanol, Ethanol, and 1-Propanol

TPD results for each of these alcohols have shown that they are unreactive when compared with 2-propanol and 2-methyl-2-propanol. After evacuation, methanol is adsorbed at a coverage of one molecule per Al and only methanol is observed in desorption (*1*, *3*). Ethanol and 1-propanol are more difficult to evacuate to a coverage of one molecule per Al, but the additional alcohol molecules desorb in a separate low-temperature state (*1*). A fraction of the more strongly adsorbed molecules undergo C–O bond cleavage during desorption, with approximately 10% of the ethanol and 40% of the 1-propanol desorbing as olefin products and water.

IR results for methanol have been discussed previously but are reviewed in Fig. 7 (*3*). The absence of the 3605 cm^{-1} peak in Fig. 7a shows that adsorption occurs at the Al sites. The C–H stretches between 2800 and 3000 cm^{-1} and the asymmetric methyl bend at 1460 cm^{-1} are indicative of unreacted methanol. We did not observe a symmetric methyl bend or a C–OH bending mode. Following exposure of the adsorbed alcohol to D_2O, the hydroxyl peaks are substituted by O–D groups, but no other changes were observed.

The results for ethanol are shown in Fig. 8a. The C–H modes in the region 2800 to 3000 cm^{-1} indicate that this alcohol also remains unreacted. Vibrational modes at 1500, 1450, and 1390 cm^{-1} are assigned to a C–OH bending mode and to the asymmetric and symmetric C–H bending modes. While the C–OH mode at 1500 cm^{-1} is slightly higher than expected, this peak disappears when the adsorbed alcohol is exposed to D_2O, as shown in Fig. 8b.

Figure 9 shows the IR spectra of adsorbed 1-propanol at different temperatures. Even after the sample is heated to 475 K, a temperature at which the majority of the adsorbed 1-propanol has desorbed from the sample, no changes occur in the C–H stretching region. As shown in Fig. 10, exposure of D_2O to adsorbed 1-propanol, even at high temperatures, leaves the C–H stretching region unchanged and results in the formation of only a small peak in the C–D stretching region. These results indicate that, unlike 2-propanol and 2-methyl-2-propanol, 1-propanol does not form an adsorbed intermediate which is susceptible to C–H/D exchange.

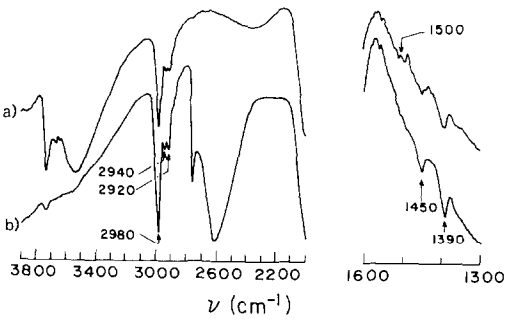


FIG. 8. Ethanol adsorbed on H-ZSM-5 before (b) and after (a) exposure to D_2O at 295 K.

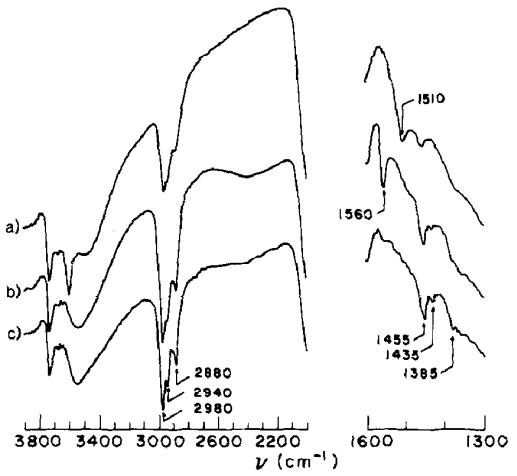


FIG. 9. 1-Propanol adsorbed on H-ZSM-5 at 295 K (c), at 375 K (b), and at 475 K (a). No changes are observed in the C–H stretching region, even after heating to high temperatures.

While the C–H stretching region of the spectrum of adsorbed 1-propanol is unchanged through the entire temperature ramp, the low-wavenumber region of the spectrum is more complex and shows that care must be taken when assigning peaks in this region to particular vibrational modes. At 295 K, three peaks appear between 1455 and 1385 cm^{-1} which are characteristic of the asymmetric and symmetric C–H bends. All three peaks are unchanged by exposure to D_2O. When the sample is heated to 375 K, a new peak forms at 1560 cm^{-1}, which is also unaffected by D_2O. Further heating of the sample to 475 K results in the disappearance of this peak and the formation of a new peak at 1510 cm^{-1}. The peak at 1510 cm^{-1} involves the hydroxyl group since it shifts to 1470 cm^{-1} upon D_2O exposure. Peaks at 1560 and 1510 cm^{-1} have been observed previously by others for alcohols adsorbed on H-ZSM-5 and have been assigned to asymmetric O–C–O stretches, surface aromatic structures, and electron-deficient C=C double bonds (*11–13*). In our experiments, however, both the C–H stretching spectra and the TPD product distribution indicate that adsorbed 1-propanol is unreacted, even at high temperatures. Caution should be used in interpreting peaks in the low-frequency region.

1-Butanol

The TPD–TGA results for 1-butanol on H-ZSM-5 are rather complex and are therefore repeated in Fig. 11. Starting with a coverage of two 1-butanol molecules per Al atom, a substantial fraction of even the second molecule is able to react. The rapid rise in the water desorption feature at 400 K, a temperature at which the coverage is still approximately two molecules per Al atom, suggests that the adsorbed molecules react to form dibutyl ether. Because of the bulkiness of dibutyl ether, only a small amount is able to desorb from the sample as dibutyl ether before undergoing further reaction to butene and higher-molecular-weight olefins.

The IR spectra for 1-butanol on H-ZSM-5 support this picture. In Fig. 12, no changes are observed in the C–H stretching region of 1-butanol, even for temperatures at which olefins were found to desorb from the sample. Since the 1-butyl alkyl groups in the ether are similar to those in the alcohol molecules, this similarity is consistent with the ether formation mechanism suggested by the TPD results. Also, adsorption of D_2O at reaction temperatures results in no changes in the C–H stretching region

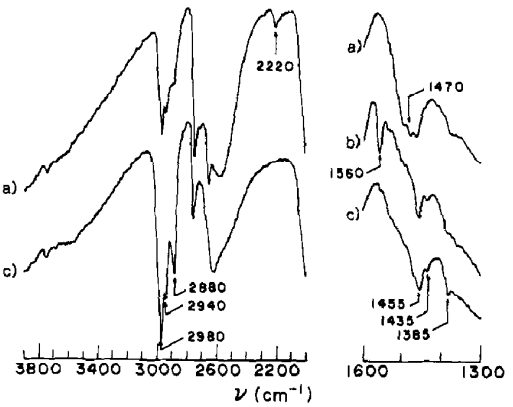


FIG. 10. 1-Propanol adsorbed on H-ZSM-5 after exposure to D_2O at 295 K (c), at 375 K (b), and at 475 K (a).

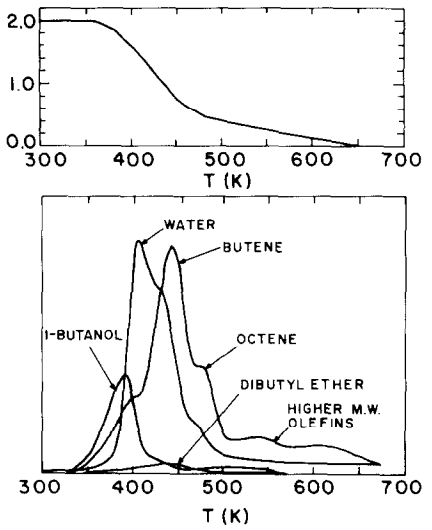


FIG. 11. TPD and TGA results for 1-butanol adsorbed on H-ZSM-5. Small amounts of 1-butanol and dibutyl ether desorb from the sample unreacted. The majority of the 1-butanol reacts to form olefin products and water.

and the formation of only a small peak in the C–D stretching region. These results are again very different from those for 2-methyl-2-propanol and 2-propanol and imply that 1-butanol does not form a new, carbenium ion-like intermediate when it reacts.

As with 1-propanol, the low-wavenumber region of 1-butanol at different temperatures is complex. At 295 K, peaks characteristic of various asymmetric and symmetric C–H bends are observed between 1465 and 1385 cm^{-1}, with an additional peak at 1500 cm^{-1}. The vibrational mode responsible for the 1500 cm^{-1} peak involves the O–H group of the adsorbed alcohol since this peak disappears following D_2O adsorption (Fig. 13). No significant changes are observed in the low-frequency region until 475 K, at which temperature a new peak appears at 1510 cm^{-1}. At 475 K, the species on the surface should have a stoichiometry close to that of dibutyl ether. The peak at 1510 cm^{-1} is also different from the one observed at 1500 cm^{-1} at 295 K since it shifts by approximately 40 cm^{-1} following D_2O adsorption and does not disappear. This new feature may result from the bending mode of a protonated ether, but no firm assignment can be made.

DISCUSSION

Zeolites are generally regarded as strong Brønsted acids (*14*). Therefore, important goals have been to provide quantitative measures of zeolite acidity and to directly observe proton transfer to adsorbates inside zeolite cavities. We believe that our

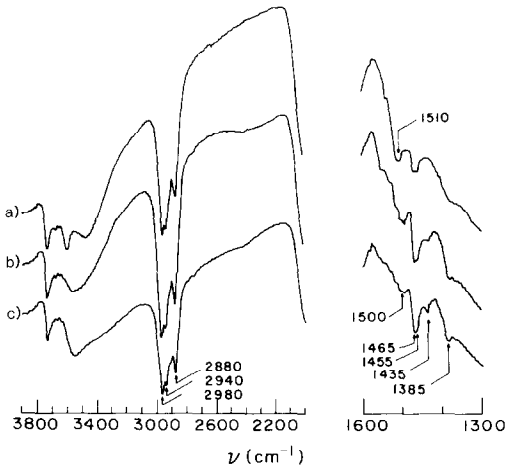


FIG. 12. 1-Butanol adsorbed on H-ZSM-5 at 295 K (a), at 375 K (b), and at 475 K (a). No changes are observed in the C–H stretching region, even at elevated temperatures.

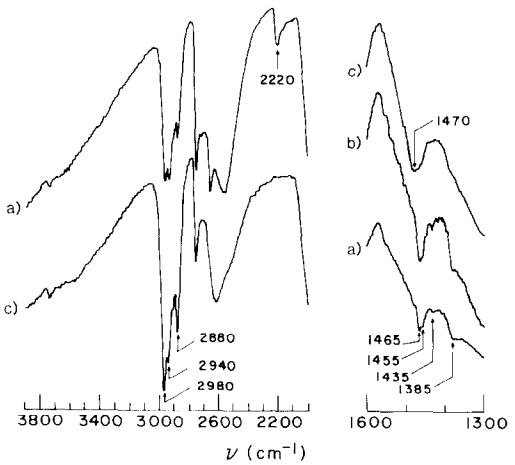


FIG. 13. 1-Butanol adsorbed on H-ZSM-5 following exposure to D_2O at 295 K (a), at 375 K (b), and at 475 K (c).

TPD–TGA studies previously reported (*1*), along with the IR experiments reported here, provide useful information in meeting both of these objectives. The chemical mechanism that we will use to rationalize observations on alcohol/H-ZSM-5 interactions is summarized as

$$\mathrm{HROH} + \mathrm{ZOH} \overset{k_{-1}}{\rightleftharpoons} \mathrm{HROH_2^+} + \mathrm{ZO^-} \underset{k_2}{\rightleftharpoons}$$
$$\mathrm{HR^+} + \mathrm{H_2O} + \mathrm{ZO^-} \rightleftharpoons \mathrm{R} + \mathrm{H_2O} + \mathrm{ZOH}. \quad (1)$$

When k_2 is rate limiting, this is the classical E_1 mechanism for proton-catalyzed alcohol dehydration (*15*). All reactions in this scheme were written as reversible processes; however, k_2 may be irreversible since H_2O can be removed from H-ZSM-5 under some experimental conditions.

In this paper and the preceding one (*1*), we have presented a number of observations which support this picture. These may be summarized as follows:

(1) Upon exposure to alcohol and removal of weakly bound molecules by pumping or heating, all HROH/H-ZSM-5 adsorption complexes form a metastable state with a stoichiometry of 1 alcohol/Al in the zeolite framework.

(2) The IR spectroscopy of this 1 : 1 complex for methyl, ethyl, 1-propyl, and 2-propyl alcohols is characterized by the appearance of C–H(D) stretching and bending modes at frequencies similar to those of the free alcohols; however, bands associated with the hydroxyl functionalities are significantly different from gas-phase molecules. These species chemisorb by interaction of the alcohol hydroxyl groups with the acidic zeolite hydroxyl groups, as evidenced by the disappearance of the sharp ZOH(D) stretch at 3605 cm^{-1}.

(3) For 2-methyl-2-propanol chemisorbed at 295 K, both C–H(D) and O–H(D) frequencies in the complex are significantly different from the free alcohol. The observed spectrum is in reasonable agreement with assignments for the t-butyl carbenium ion in FSO_3H–SbF_5–SO_2 solutions (*10*).

(4) On heating, the methyl, ethyl, and 1-propyl complexes lose intensity in all spectral features uniformly. TPD shows that all these primary alcohols desorb largely intact from the 1 : 1 complexes, consistent with the decomposition of the adsorption complex by reaction k_{-1}. The 2-propyl complex, on the other hand, undergoes significant changes in its C–H(D) stretching and bending features at approximately 360 K before any appreciable desorption occurs. The spectrum observed after this secondary alcohol/zeolite complex is heated is very similar to that formed directly on chemisorption of the tertiary alcohol, 2-methyl-2-propanol, at 295 K. Desorption curves for both the secondary and tertiary alcohol/zeolite complexes yield only water and olefins.

(5) The intermediates formed from 2-methyl-2-propanol at 295 K and from 2-propanol at 360 K, but no other adsorbate structures from any other alcohol, undergo H/D exchange incorporating isotopic species into all C–H(D) bonds.

(6) On desorption of all of the alcohols, the sharp ZOH(D) stretching band returns.

In reaction (1), the two types of adsorbed intermediates have been depicted as oxonium ions ($HROH_2^+$) and carbenium ions (HR^+), respectively. This is not intended to imply that the zeolite-bound intermediates are "free" organic ions. All ions interact with the medium in which they are formed (*16*). However, we believe that it is useful, as a general formalism for systematizing observations on ion thermochemistry and structure, to consider the medium effects as a perturbation on the properties of the free ions. For example, in a previous paper, we showed that the relative stabilities of gas-phase ions correlate well with the apparent stabilities of intermediates in H-ZSM-5 (*1*). This implies that one can change the structure of the alcohol without significantly changing the interaction energy. Our discussion of the spectral data on these intermediates will again consider the effect of the zeolite framework to be nonspecific and

will again discuss spectral features for the adsorbates by comparison to their appearance in noninteracting media.

It is important to point out that the general structure/activity profile that we observe for alcohols in H-ZSM-5 mirrors what has been reported for alcohols in FSO_3H/SbF_5 solutions, where a variety of spectroscopic evidence has been employed to support the sequential oxonium ion–carbenium ion mechanism. In magic acid solutions, the alcohol chemistry may be summarized as follows: Tertiary carbenium ions form rapidly and are the first species observed at 210 K; secondary carbenium ions form by loss of water from the protonated alcohol on warming to 240 K; primary carbenium ions can be obtained from 1-butanol at 290 K, but methanol and ethanol remained undissociated to much higher temperatures (*17*).

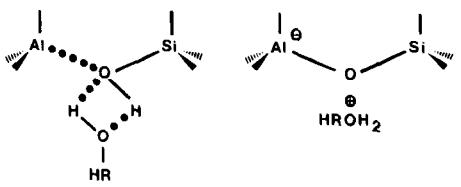
Oxonium Ions

In the case of the oxonium ions, the data demonstrate that the adsorbed alcohol molecule is intact. The C–H modes are relatively unperturbed, but the OH functionalities of the alcohol and zeolite interact strongly. One might consider two limiting descriptions of the hydroxyl interaction (Scheme 1). At one extreme, the alcohol molecule is hydrogen-bonded to the framework but the proton remains associated primarily with the zeolite. At the other extreme, the proton is fully transferred and the structure is best described as an ion pair. In effect, the question involves the description of the potential surface for proton transfer between the two conjugate bases, ZO^- and HROH. We are unable to distinguish between these extremes with the current spectral information. However, the chemisorption energies for these alcohols in H-ZSM-5 are in the range 15–30 kcal/mol (*18*). If the bulk of this energy is associated with the hydroxyl group interactions, then the ion-pair structure should probably be preferred. In homogeneous systems, it has been argued that hydrogen bond energies between two uncharged molecules are unlikely to exceed 7 kcal/mole and higher interaction energies represent ion pairing (*19*).

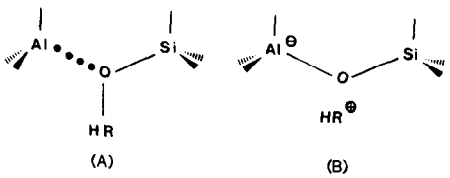
Carbenium Ions

As we have done for the oxonium ion, we may think of two limiting structures for the dehydrated complex. These are pictured in Scheme 2. In **(A)**, there is no formal charge on the organic moiety. The structure may be best described as a silyl ether coordinated through oxygen with the neighboring Lewis acidic aluminum atom. In **(B)**, full formal charges are developed on the framework and the adsorbate. One may say that in structure **(A)**, the zeolite framework is acting like a nucleophilic medium and interacting with the adsorbed cation via specific bond formation, whereas, in structure **(B)**, the zeolite is nonnucleophilic and is interacting nonspecifically. The relative stabilities of these structures are likely to be a function of R. For example, one is inclined to picture Na-ZSM-5 as structure **(B)** and H-ZSM-5 as structure **(A)**.

For the carbenium ion-like adsorbates, the properties of the corresponding ions in SbF_5 solution constitute a useful model for structure **(B)**. Because of the absence of nucleophilic trapping agents in these solutions, long-lived carbenium ions have been



SCHEME 1



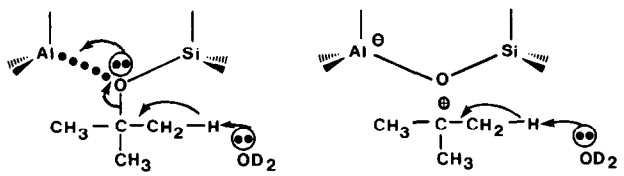
SCHEME 2

prepared and spectroscopically characterized (*20*). The methyl stretching and bending frequencies of the t-butyl group adsorbed in H-ZSM-5 are similar to those of t-butyl carbenium ions in SbF_5, as reported by Olah *et al.* (*10*). This similarity and the loss of the *gem*-dimethyl bending on adsorption, are both suggestive of a structure like **(B)**, where the organic adsorbate develops substantial charge and deviates from tetrahedral geometry at the central carbon. One might expect the IR spectrum of a species like structure **(A)** to be more similar to the parent alcohol. SbF_5 solution models have also been used by Kramer *et al.* to discuss energy barriers to intramolecular rearrangements of tertiary carbenium ions in ultrastable Y-zeolites (*21*). They conclude, in a similar fashion to what we suggest from our IR and structure/activity data, that the zeolite framework in these high silica systems constitutes a relatively nonnucleophilic medium for the formation and reaction of carbenium ions.

The H/D exchange can be interpreted by reversible formation of an olefin in the presence of added water. From an intermediate like **(B)**, D_2O would act as the base in the second step of an E_1-type reaction sequence [i.e., **(D)** in Scheme 3]. From an intermediate like **(A)**, deprotonation would be accompanied by cleavage of the bond to the zeolite framework in an E_2-type sequence [i.e., **(C)** in Scheme 3]. In either case, deprotonation must be thermodynamically unfavorable, and return to the stable carbenium ion-type structure by D^+ transfer allows incorporation of deuterium into the hydrocarbon chain without any net chemical change. It is known that 2-propyl carbenium ions undergo rapid intramolecular scrambling of both their C and H atoms in SbF_5 solutions at temperatures as low as 185 K (*22*). This demonstrates that, in the "free" carbenium ion, these C–H bonds are very labile. In solution, these scrambling reactions are thought to proceed via protonated cyclopropane intermediates. The protonated cyclopropane intermediates are necessary to explain the observation that all protons and carbon atoms in the carbenium ion scramble equivalently, even though they are not equivalent in the open-chain 2-propyl carbenium ion structure. Similar processes may take place in the zeolite, since it appears that all C–H bonds incorporated deuterium. Exchange experiments of this kind were first used many years ago to study intermediates on silica–alumina surfaces (*23*).

Several elements of the data are not completely explained by this picture. For example, we observe that it is more difficult to exchange the protons in the 2-propyl complex than in the t-butyl complex, even though on the basis of carbenium ion structures, the energy required to form an olefin should be smaller. This may indicate that the 2-propyl system interacts more strongly with the zeolite framework. That is, for 2-propyl, the adsorbate structure looks more like **(A)** and there is therefore an additional barrier to exchange associated with the cleavage of the adsorbate-framework bond as in **(C)**.

The proton transfer reaction depicted in



(C) (D)

SCHEME 3

$$(CH_3)_3C^+ + D_2O \rightarrow (CH_3)_3C{=}CH_2 + HD_2O^+ \quad (2)$$

is endothermic by about 24 kcal/mol in the gas phase (*24*). The rapid H/D exchange that we have observed at room temperature suggests that this reaction must be more favorable in the zeolite. In other words, the products in reaction (2) must be stabilized relative to the reactants by interactions with the reaction medium. We speculate that water present in the zeolite pores during an exchange reaction could have a significant influence on the thermochemistry. Specifically, ambient water may stabilize the hydronium ion, H_3O^+. The stabilization that results from the addition of H_2O to H_3O^+ to form $H_5O_2^+$ is large and much more important than the corresponding stabilization of a bulkier, more polarizable ion like $(CH_3)_3C^+$, especially in the hydrophobic environment of an H-ZSM-5 cavity (*25*).

It is not clear at what point in our scheme the known oligomerization chemistry of the olefins begins to intervene. The H/D exchange results imply that olefins are accessible from the carbenium ion-like intermediates at low temperatures in the presence of additional H_2O. We have argued based on the absence of AlOH and olefinic features in the IR that these olefins are not mobilized until desorption temperatures are reached. More work is underway to clarify these aspects of the extended mechanism.

1-Butanol

The observations on 1-butanol cannot be rationalized within the context of the model we have applied to the data on the other alcohols. Unlike the other alcohols, 1-butanol shows no evidence for formation of a discrete adsorption complex of 1 : 1 stoichiometry at acid sites. Its desorption spectrum and IR characteristics are more complex. It shows no deuterium exchange, even at temperatures where product olefins have begun to desorb. These observations are consistent with the increasing importance of bimolecular dehydration in the 1-butanol chemistry.

A comparison of these results for the dehydration of the different alcohols with solution-phase chemistry is instructive. In the reaction of alcohols with hydrogen halides to form alkyl halides, secondary and tertiary alcohols undergo reaction through an SN_1 mechanism involving a carbenium ion intermediate. The alkyl group normally rearranges during reaction to form the most stable carbenium ions. Primary alcohols, however, react predominantly through an SN_2 mechanism and no rearrangement of the alkyl group is usually observed (*15*, pp. 331–336). This change in mechanism is consistent with differences we observe in the dehydration chemistry for 1-butanol compared with that for 2-propanol and 2-methyl-2-propanol. The reason for 1-butanol being more reactive than the other primary alcohols in our study is probably related to increased interactions between the longer hydrocarbon chain and the organophilic zeolite walls. This interaction presumably maintains the coverage of 1-butanol at two molecules per Al site to a high enough temperature for the bimolecular reaction to occur. Undoubtedly, this variation on the mechanism is important for the dehydration of other alcohols on H-ZSM-5 under typical catalytic reactor conditions.

SUMMARY

The IR spectra of adsorbed alcohols on H-ZSM-5 corroborate the conclusions of previous TPD–TGA work which viewed the principal interaction in chemisorption as proton transfer from the zeolite framework to the alcohol (*1*). The nature of the zeolite/adsorbate interaction is a strong function of the alcohol structure and the temperature. The adsorbed species may be modeled as ion pairs consisting of oxonium ions or carbenium ions coupled with the anionic zeolite framework. The spectral features and isotopic exchange capabilities of the adsorbed molecules agree well with

those of ions formed in relatively nonnucleophilic, acid media.

ACKNOWLEDGMENT

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