Adsorption and Reaction of 2-Propen-1-ol in H-ZSM-5†

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The adsorption of 2-propen-1-ol in H-ZSM-5 has been studied by temperature-programmed desorption (TPD), thermogravimetric analysis (TGA), and transmission infrared spectroscopy. Following adsorption at 295 K, an adsorption complex with a stoichiometry of 1 2-propen-1-ol molecule/Al site can be easily identified in TPD-TGA. This 1:1 complex reacts above 360 K to form water and an allylic intermediate that undergoes secondary reactions to form simple olefins and aromatics before leaving the zeolite. Infrared spectra of the intermediate at various temperatures indicate that the intermediate is highly reactive, and the spectra are consistent with the formation of an alkyl silyl ether species during reaction. However, the ease of forming dehydration products from the 1:1 adsorption complex with 2-propen-1-ol compared to that for other alcohols is well described by the relative gas-phase stability of the carbenium ions, implying that formation of the carbenium ion must be an important step in the reaction.

Introduction

In order to determine the structure and stability of hydrocarbon intermediates in zeolites, we have been studying the adsorption and transformation of simple alcohols in high-silica zeolites.[1,2] For many simple alcohols, we have shown that well-defined adsorption complexes can be formed with a stoichiometry of 1 molecule/framework Al in H-ZSM-5, H-ZSM-12, and H-mordenite.[3,4] In the case of the secondary and tertiary alcohols, 2-propanol and 2-methyl-2-propanol, these 1:1 adsorption complexes undergo a unimolecular, Brønsted-acid-catalyzed decomposition to form olefins and water. Since 2-methyl-2-propanol reacts at 295 K and the water produced can be removed from the zeolite by evacuation, stable intermediates can be formed, in a stoichiometry of 1 molecule/Al, which can be studied spectroscopically.[5]

By comparing the reactivity of a series of alcohols during temperature-programmed desorption (TPD) from H-ZSM-5, we were also able to develop a semiquantitative model of zeolite acidity.[2] The model assumes that the main interaction between an adsorbed molecule and the acid site involves proton transfer from the zeolite. On heating, the proton-bound alcohol either dehydrates or desorbs unchanged. The choice between these pathways is controlled by the relative energies of proton transfer and carbenium ion formation. The model works very well for explaining the relative reactivities of each of the alcohols and can even be used to predict heats of adsorption for simple aromatics and to explain the relative reactivities of propene and ethene in H-ZSM-5. While the model assumes that stable carbenium ions can be formed by adsorption of secondary or tertiary olefins, subsequent ^{13}C NMR studies have shown that simple olefins are, indeed, protonated but are covalently rather than ionically bound to the zeolite lattice.[6,7] However, the relative reactivities of the various adsorbates imply that carbenium ion stabilities still dominate the reaction rates.

In the work described in this paper, we have extended the range of simple alcohols that we have examined and further tested the predictive capabilities of the zeolite acidity model by studying the adsorption of 2-propen-1-ol in H-ZSM-5. This probe molecule was chosen because the allyl carbenium ion is resonance stabilized and almost as stable as the 2-propyl ion. As with most of the other simple alcohols, a well-defined, 1:1 adsorption complex can be identified with 2-propen-1-ol. This 1:1 complex reacts to form water and a hydrocarbon intermediate at a temperature that is close to that necessary to react 2-propanol, in agreement with predictions of the acidity model. Secondary products from propene to aromatics dominate the TPD results, implying that the bound allylic species is highly reactive and may be important in the formation of aromatics under reaction conditions.

Experimental Section

The equipment used in the TPD-TGA experiments has been described in previous papers.[2,8] The apparatus consisted of a Cahn Model 2000 microbalance mounted in a chamber that could be evacuated below 10^{-7} Torr with a turbomolecular pump. Approximately 15–17 mg of zeolite was spread over the microbalance sample pan and could be heated linearly to approximately 750 K by a temperature programmer. The heating rate used in all of these experiments was 10 K/min. A mass spectrometer, multiplexed by a microcomputer, was attached to the system to monitor the species desorbing from the sample. Alternatively, the desorbing gases in any temperature region could be collected in a cold trap and expanded into the gas-sampling valve of a gas chromatograph. Tests demonstrating the efficiency of this method for collecting and identifying samples have been discussed elsewhere.[8]

Infrared spectra were obtained with use of a grating-type spectrophotometer and a sample cell similar in design to one used in previous studies.[5] The cell contained a self-supporting, 35-mg wafer, 1.6 cm in diameter, and allowed the sample to be evacuated by a liquid-nitrogen-trapped mechanical pump. It was found that a clean sample could be maintained under these conditions for many hours. The sample could also be heated to roughly 750 K, with the temperature being measured by a thermocouple soldered to the tube holding the wafer. To avoid having the IR beam affect results, exposure to adsorbates and sample heating were always performed with the sample out of the IR beam. The procedure for heating the sample involved ramping the temperature to the final value indicated, holding at that temperature for several minutes until the pressure returned to the base pressure, and cooling back to room temperature before placing the sample in the infrared beam. Previous TPD measurements of 2-propanol from the zeolite wafer in the IR cell and in the TPD-TGA apparatus gave results that were very similar. Evolution of propene and water occurred at the same temperature in both sets of experiments, showing that the temperatures of the IR sample were

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TABLE I: Products Formed in Various Temperature Ranges during TPD as Measured by Gas Chromatography

	295–385 K	385–405 K	405–435 K	435–530 K	600–685 K
2-propen-1-ol	90.7	27.00	0	0	
C_2H_4	0	0	1.7	18.5	15.9
C_3H_6	1.6	60.3	96.6	51.4	41.3
C_4	2.8	3.7	0	6.9	2.1
C_5	0	0	0	1.9	2.2
benzene	0	3.7	0	3.3	18.7
toluene	0	0	0	12.6	6.5
C_8	3.0	3.2	1.6	1.7	4.5
C_9	0	0	0	2.9	4.6
C_{10}	0	0	0	0	1.9

accurate, even though they were measured indirectly.[1] However, the evacuation conditions in the IR cell were not as rigorous as those that were used in the TPD-TGA apparatus. While the infrared spectra provide complimentary evidence for determining what is in the zeolite at various stages during TPD, secondary oligomerization reactions were somewhat more important in the IR experiments.

Several different ZSM-5 samples were used, with most of the work having been carried out on two samples having a SiO_2/Al_2O_3 ratio close to 70. The first of these samples, H-ZSM-5(1), was obtained from the Mobil Oil Company and consisted of particles that were uniform spheres approximately 0.5 μm in diameter. The second, H-ZSM-5(2), was synthesized in hydrothermal solution with a TPA-Br template and had particle sizes between 0.1 and 1.0 μm. Prior to performing experiments, each sample was converted to the hydrogen form by ammonium ion exchange, followed by heating in vacuum to above 700 K. Each sample was characterized by X-ray diffraction and *n*-hexane uptakes. The *n*-hexane uptakes gave pore volumes of 0.175 and 0.178 cm^3/g for the H-ZSM-5(1) and H-ZSM-5(2) samples, respectively, which are reasonably close to the ideal pore volume of 0.19 cm^3/g for ZSM-5. All of the infrared spectra shown in this paper were obtained on the H-ZSM-5(2) sample, and the chromatographic measurements were only carried out on H-ZSM-5(1). TPD-TGA experiments were also carried out on a third sample, H-ZSM-5(3), which had a SiO_2/Al_2O_3 ratio of 520 to determine the effect of Al concentration. Characterization of this sample has been discussed elsewhere.[3]

Results

The TPD-TGA results following exposure of the H-ZSM-5(1) and the H-ZSM-5(2) samples to 11 Torr of 2-propen-1-ol at 295 K and approximately 1-h evacuation are shown in Figures 1 and 2. The chromatographic analysis of the products for H-ZSM-5(1), in various temperature ranges, are shown in Table I. The initial coverages corresponded to more than 1 molecule/Al site and were dependent on evacuation time and the particular zeolite sample that was being investigated. However, all 2-propen-1-ol (m/e = 57) in excess of 1 molecule/Al desorbed unreacted in a desorption feature centered at $\sim$370 K and all of the alcohol below a coverage of 1 molecule/Al reacted to give water and a mixture of hydrocarbon products. These observations were also found for the H-ZSM-5(3) sample, further demonstrating that the dehydration chemistry in these experiments is occurring at the Al sites.

Water (m/e = 18) desorption occurred in two major peaks, the first between 370 and 400 K and the second between 400 and 430 K. Since water can be removed from H-ZSM-5 by evacuation at 295 K in our system,[2] these desorption features are at least partially reaction rate limited. The relative area under these two peaks was sample-dependent. For the H-ZSM-5(1) in Figure 1, the lower temperature feature was dominant and the higher temperature peak was only a small shoulder on the main feature. For H-ZSM-5(2) in Figure 2, the two peaks were almost equal in size. While no hydrocarbons were observed desorbing along with the first water feature, propene (m/e = 41) desorbed simultaneously with the second water peak, except that the propene feature was shifted to slightly higher temperatures. That the hydrocarbon product between 410 and 440 K was almost pure propene, and not a mixture of olefins, was confirmed by GC analysis, as shown in Table I. Also, it can be seen that the amount of propene scaled with the amount of water present in the higher temperature peak, suggesting that the water and propene evolve from a single chemical event. It should be noted, however, that the sensitivity of the m/e = 18 peak for water and m/e = 41 peak for propene are not the same. The relatively small weight change between 410 and 440 K in the TGA results shows that the amount of propene desorbing between 410 and 440 K must be considerably smaller than the amount of water leaving the sample in this temperature range, since the total amount of water must correspond to 1 molecule/Al. The fact that propene evolves from the sample, not allene, shows that this event must be preceded by a bimolecular reaction. This also implies that the second water

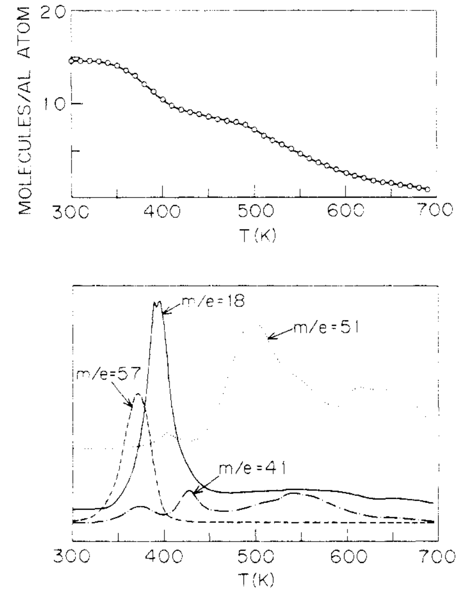

Figure 1. TPD-TGA curves for 2-propen-1-ol from the H-ZSM-5(1).

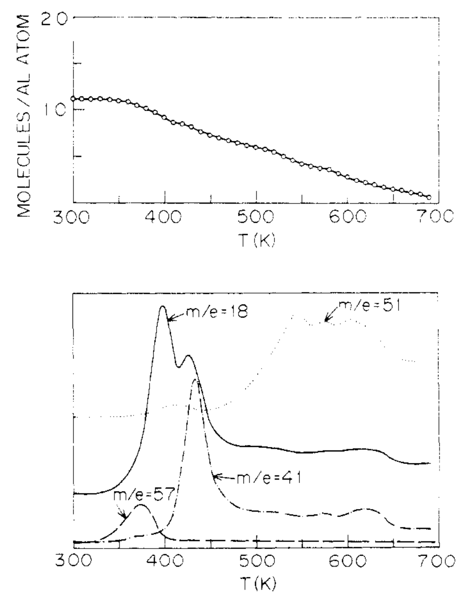

Figure 2. TPD-TGA curves for 2-propen-1-ol from the H-ZSM-5(2).

TABLE II: Observed IR Spectral Features for 2-Propen-1-ol on H-ZSM-5

temp, K	spectrum[a]	ν(=C—H)	ν(-C—H)	ν(C=C)	δ(C—H)	unknown
rt[b]	a	3100–3030 3090	2860 2940 2985	1640	1430	
295	b	3090	2880 2940		1460 1420	1540
350	c	3090	2880 2940 2970		1460 1420	1540
400	d	3090	2880 2940 2970	1600?	1460 1420	1540
430	e	3090	2880 2940 2970	1600?	1460 1420	1540
550	f	3090	2850–3000	1600?	1460 1420	1500

[a] Letters correspond to spectra in Figure 3. [b] rt = room temperature; liquid.

desorption feature is probably not due to a second type of adsorption site with a different acid strength.

The results on H-ZSM-5(3) were qualitatively similar. Only water and hydrocarbon products were observed for a coverage of 1 molecule/Al, and the water formed at the same temperature found for the other two samples. Also, even for the low Al concentration of this sample, no allene was observed in the products, indicating that secondary chemistry still dominated the hydrocarbon products. A propene peak at ~430 K was still observed, although the fraction of the hydrocarbon products that went to form propene at this temperature was now much smaller than for the other two samples.

Most of the products formed from reacting 2-propen-1-ol are removed above 450 K as a complex mixture, with considerable quantities of light aromatics being formed ($m/e = 51$). Chromatographic analysis of the desorbing mixture shows that the aromatics are predominantly benzene, toluene, and xylene. Since benzene and toluene[9] are known to desorb below 400 K under the conditions of our experiment, the evolution of these aromatics at high temperatures must be controlled by secondary reactions, either the decomposition or combination of more stable species present in the zeolite. Finally, some products could not be removed thermally, as shown by the fact that the zeolite sample weight did not return to the initial value prior to adsorption. *n*-Hexane uptakes following TPD experiments decreased slightly from that measured on the clean zeolite, showing that at least some of the residue is in the zeolite pores. This residue had to be burned off the sample by heating it in air before beginning the next adsorption experiment.

In order to characterize the intermediates formed in the zeolite, we measured the infrared spectra, shown in Figure 3, after adsorbing 2-propen-1-ol and heating in vacuum to the indicated temperature. As discussed previously, all spectra were measured after the sample had cooled to room temperature to avoid IR beam heating. Table II lists all of the observed features and compares them to spectral features previously reported for allyl alcohol and the allylic carbenium ion. Figure 3a shows the spectrum of clean H-ZSM-5. The hydroxyl stretching peaks at 3740 and 3605 cm^{-1} have been assigned to external silanol groups that terminate the particles and hydroxyl groups associated with the Al sites, respectively.[10]

After the zeolite is exposed to 2-propen-1-ol and is evacuated for 2 h, the spectrum in Figure 3b is obtained. The spectrum in Figure 3c was measured after the sample had been heated to 350 K to remove any excess 2-propen-1-ol above a coverage of 1 molecule/Al. The features in both spectra are essentially the same. As with other alcohols adsorbed in H-ZSM-5,[5] the hydroxyl peak at 3740 cm^{-1} is unaffected by adsorption of 2-propen-1-ol, but the hydroxyl stretch at 3605 cm^{-1} has been replaced by a broad band centered at ~3530 cm^{-1}, indicating strong coupling of the Al hydroxyls to the alcohol hydroxyls. Since the alcohol coverage is close to 1 molecule/Al, this coupling implies that the alcohol molecules are present at the Al sites. The ν(C–H) region between 2800 and 3200 cm^{-1} is very similar to that of liquid 2-propen-1-ol. A peak at 3095 cm^{-1} due to ν(C–H) with olefinic C atoms is clearly present, and while the peaks between 2800 and 3000 cm^{-1}

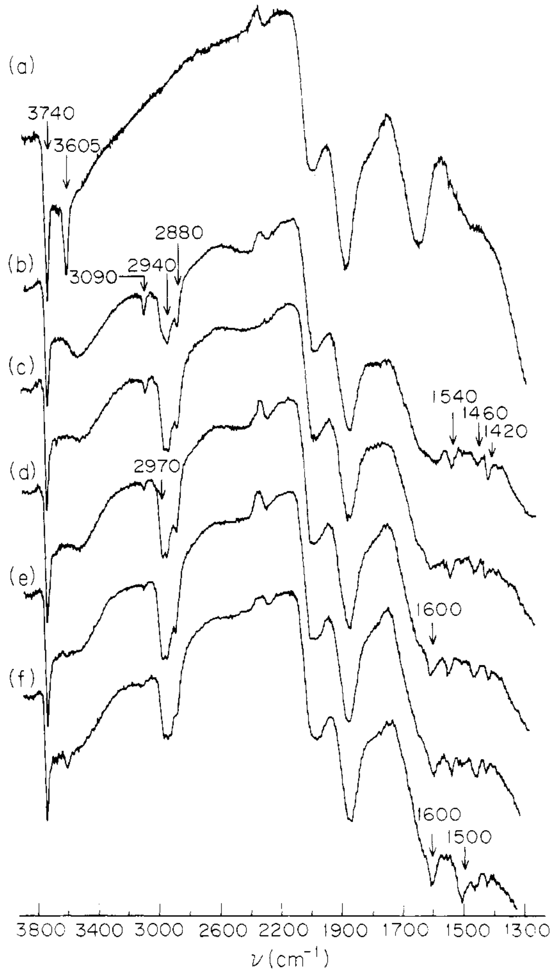

Figure 3. IR spectra for 2-propen-1-ol on H-ZSM-5(2) after heating in vacuo to the following temperatures: (b) 295, (c) 350, (d) 400, (e) 450, and (f) 550 K. Spectrum a is of the clean H-ZSM-5. The inverted peak between 2300 and 2400 cm^{-1} is from CO_2 in the reference beam.

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on the zeolite are poorly defined and broadened compared to those peaks in the same region for the liquid, the peak positions and relative intensities are very similar to that of the pure liquid. The presence of peaks due to olefinic species implies that the hydroxyl function, and not the olefinic function of 2-propen-1-ol, interacts most strongly with the zeolite acid sites, as expected based on proton affinity considerations.[15] It should be noted that the intensity of ν(C–H) peaks for olefins are usually much weaker than for aliphatics and that the relative intensities of these spectral regions are not indicative of the relative concentrations of these different species. Peaks due to δ(C–H) bending modes at 1420 and 1455 cm^{-1} can also be identified. Liquid 2-propen-1-ol has a ν(C=C) stretch at 1640 cm^{-1} that is difficult to observe on the zeolite due to the interference of a zeolite framework band at the same frequency. Additional bands at 1540 and 1600 cm^{-1} are present in spectra b and c that are not present in the liquid alcohol. Bands at ~1540 cm^{-1} are often assigned to a ν(C–C) stretch of an allylic species.[11,12] However, other IR spectral features and the TPD results are not consistent with dehydration of the alcohol below ~360 K, and a previous IR study has pointed out that it is often difficult to assign features in this region of the spectrum unambiguously.[5]

Parts d–f of Figure 3 show the IR spectrum obtained after heating to various temperatures. One should first notice that, even after heating to 550 K, the intensity of the 3605-cm^{-1} peak is still significantly smaller than it is for the clean surface, implying a high adsorbate coverage. Since the TGA results in Figure 2 indicate that the adsorbate coverage was low at this temperature in the TPD-TGA measurements, the conditions used for evacuation in these two sets of measurements must significantly affect what is present in the zeolite. That secondary reactions are to be expected has already been demonstrated from the TPD results, and the less rigorous evacuation procedure used in the IR measurements apparently results in these secondary reactions being more extensive.

The changes observed in the IR with heating were not dramatic up to 430 K. The spectra show a decrease in the peak at 3095 cm^{-1}, an increase in the peak at 2970 cm^{-1}, and better definition of the peak at 1600 cm^{-1} but are otherwise similar to spectra of the unreacted alcohol in b and c. Since all of the water formed by dehydration of the alcohol should have been removed by holding the sample at 430 K, we interpret the fact that there are no dramatic changes in the spectra as implying that no new functional groups, such as carbenium ions, are formed. Recent ^{13}C NMR studies of *tert*-butyl intermediates formed by dehydration of 2-methyl-2-propanol in H-ZSM-5 have shown that the stable species at the Al site following dehydration is an alkyl silyl ether.[6] Assuming that covalent bonding between the adsorbate and the framework oxygen is also important with the intermediates formed by 2-propen-1-ol, the bending and stretching modes of the allylic and oligomeric intermediates should be expected to occur at the same frequencies observed for the unreacted 2-propen-1-ol.

The spectrum changes dramatically after the sample has been heated to 550 K (Figure 3f). The very intense bands at 1500 and 1600 cm^{-1} and the ν(C–H) stretch centered around 3120 cm^{-1}, along with the anticipated ratio of H/C atoms, indicate that the species in the zeolite probably include aromatics. Since there are likely to be a large number of products present under these conditions, detailed identification of peaks is not possible. However, the spectrum is in clear contrast with the lower temperature spectra, showing that the basic hydrocarbon framework of 2-propen-1-ol is no longer intact.

SCHEME I

$$H_2C{=}CH{-}CH_2OH + ZOH \longrightarrow H_2C{=}CH{-}CH_2OH_2^+\ ZO^- \quad (1)$$

$$H_2C{=}CH{-}CH_2OH_2^+ZO^- \longrightarrow H_2C{=}CH{-}CH_2^+ZO^- + H_2O \quad (2)$$

$$H_2C{=}CH{-}CH_2^+ZO^- \longrightarrow H_2C{=}C{=}CH_2 + ZOH \quad (3)$$

$$H_2C{=}C{=}CH_2 + H_2C{=}CH{-}CH_2OH_2^+ZO^- \longrightarrow (H_2C{=}CH{-}CH_2)_2OH^+ZO^- \longrightarrow H_2O + CH_3CH{=}CH_2 + \text{intermediates} \quad (4)$$

$$H_2C{=}C{=}CH_2 + H_2C{=}CH{-}CH_2^+ZO^- \longrightarrow \text{hydrocarbons} \quad (5)$$

SCHEME II

$$\begin{tikzcd}
B_g + ZOH \arrow[r, "\Delta H_{bind}"] \arrow[d, "-PA_{ZO^-}"] & BH^+\cdots ZO^- \\
B_g + H^+ + ZO^- \arrow[r, "PA_B"] & BH_g^+ + ZO^- \arrow[u, "\Delta H_{inter}"']
\end{tikzcd}$$

The TPD-TGA and IR results for 2-propen-1-ol in H-ZSM-5 are consistent with the reactions shown in Scheme I. At room temperature, 2-propen-1-ol interacts strongly with the hydroxyl group at the Al site and is at least partially protonated to form an oxonium ion, as in reaction 1. Between 370 and 400 K, the alcohol adsorbed at a coverage of 1 molecule/Al reacts to form water and an allylic intermediate at the Al site (2). (In Scheme I, the allylic intermediate is formally shown as a carbenium ion, although in reality this complex is probably better described as a covalent structure than as an ion pair.[6]) Allene is formed from the allylic intermediate (3) but is sufficiently reactive to form secondary products before leaving the zeolite. This is consistent with results obtained from 2-methyl-2-propanol, where the olefin products formed during desorption are also dominated by secondary oligomerization reactions, except for desorption from zeolites with very low Al concentrations.[7] The majority of the allene reacts with neighboring allylic intermediates to form complex products (5) containing more than three carbons that desorb above 450 K. The simultaneous formation of water and propene between 410 and 440 K suggests that some of the allene reacts with protonated alcohol during the temperature ramp to form diallyl ether (4), which then decomposes to form propene and water. While alternative steps to (4) could be suggested to explain the simultaneous formation of propene and water, a bimolecular reaction must be involved for the formation of propene. Some of the propene probably undergoes oligomerization before it can diffuse out of the zeolite. The fact that the amount of product formed in step 4 is sample-dependent could be due to mass-transfer differences in the particles or differences in the distribution of Al in the zeolite particles. This is also consistent with our observation that the fraction of 2-propen-1-ol, that reacts to form propene was significantly decreased for the sample with a higher SiO_2/Al_2O_3 ratio.

Discussion

In our previous work, we had demonstrated that stoichiometric adsorption complexes could be formed between the Al sites in H-ZSM-5 and toluene, 2-propanone, 2-propanamine, and a series of alcohols.[2,3,9,13] The results for 2-propen-1-ol adsorption further demonstrate this 1:1 chemistry and reinforce the picture that the acid sites in carefully prepared, unsteamed H-ZSM-5 are identical and in a coverage of 1 molecule/Al site.

This observation of identical acid sites in a concentration equal to the Al concentration suggested that a semiquantitative scheme could be developed to further understand the acid sites.[2] In this scheme, the adsorption of a gas-phase adsorbate (B_g) at the hydroxyl site associated with framework Al (ZOH) is separated into three simple steps as shown in Scheme II. In this hypothetical thermochemical cycle, the proton is first removed from the zeolite, then it is allowed to react with the gas-phase alcohol to form a gas-phase base (BH^+_g), and finally the protonated base is allowed to combine with the Al site (ZO^-). The advantage of looking at the adsorption process in this way is that the gas-phase heats of formation (PA_B) have been measured for a large number of bases and the proton affinity of the zeolite (PA_{ZO^-}) is a constant. If

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TABLE III: Calculated Energies for Mechanism 1 Based on Gas-Phase Proton Affinities

HROH	HROH + ZOH	$HROH_2^+ZO^-$	HR^+ZO^- + H_2O	R + ZOH + H_2O
CH_3CH_2OH	0	−20	+18	+10.9
$(CH_3)_2CHOH$	0	−21	−3	+12.2
$(CH_3)_3COH$	0	−25	−14	+12.6
CH_2CHCH_2OH	0	−19	+1	+17.4

the bonding between the zeolite and the protonated base does not depend strongly on the structure of B (ΔH_{inter} is constant), the binding energy for the adsorbate will scale directly with PA_B. This picture obviously does not account for interactions not associated with the zeolite hydroxyls, such as the strong adsorption of alkanes in high-silica zeolites.

Using this scheme and the above assumptions, one can predict the binding energy for any adsorbate if ΔH_{bind} is known for any other adsorbate. Furthermore, if one assumes that the ability of molecules to react at the acid sites is controlled by the stability of the intermediates that can be formed by decomposition of these complexes, predictions can be made of the relative reactivities of various molecules. For the alcohols, the simplest reaction would consist of the following steps:

mechanism I

$$HROH + ZOH = HROH_2^+ZO^- = HR^+ZO^- + H_2O = R + H_2O + ZOH$$

This mechanism begins with protonation of the alcohol at the acid sites in the zeolite and requires that reaction to the olefin, R, proceeds via the formation of an adsorbed carbenium ion, HR^+ZO^-. In a previous paper, the measured heat of adsorption of methanol, −15 kcal/g-mol,[14] was used to anchor this potential energy scheme and tabulated values for heats of reaction and proton affinities of both alcohols and olefins were used to calculate the enthalpies of each step in this simple sequence for a variety of alcohols.

For understanding the results with 2-propen-1-ol and comparing these results to those for other alcohols, it is useful to see how this molecule fits into the above reaction picture. The enthalpies for the steps in the reaction sequence of mechanism I are shown in Table III, along with the calculated energies for a representative series of alcohols of varying reactivity. The calculations were carried out as described previously[2] except that the heat of formation of the gas-phase, allylic carbenium ion, $\Delta H_f(BH^+)$, was used rather than the proton affinity of allene to scale HR^+ZO^-. This was necessary since the gas-phase protonation of allene results in the methyl vinyl cation, rather than an allylic carbenium ion, due to kinetic limitations.[15] Table III indicates that the adsorption energies for the unreacted alcohols are relatively insensitive to the particular alcohol being considered since the proton affinities of the alcohols do not vary significantly. The main difference between the alcohols occurs in the relative stabilities of the carbenium ions formed during reaction.

This picture explains the experimental observations well. Primary alcohols like ethanol are relatively unreactive and desorb as the alcohol under high-vacuum conditions.[2] Consistent with this, the values in Table III show that it is energetically easier for the adsorbed alcohol, $HROH_2^+ZO^-$, to decompose back to the gas-phase alcohol rather than to go on to form olefin products. In contrast, the lowest energy channel for adsorbed 2-methyl-2-propanol involves dehydration to the adsorbed *tert*-butyl carbenium ion. Experimentally, 2-methyl-2-propanol decomposes following adsorption in H-ZSM-5 and the water formed from the reaction can be evacuated at room temperature. The calculations for 2-propanol imply that the isopropyl carbenium ion should be slightly more accessible than the unadsorbed alcohol, in agreement with the experimental evidence that this alcohol reacts to propene and water during desorption. Because the reaction channels are similar in energy, dehydration does not take place below 370 K.

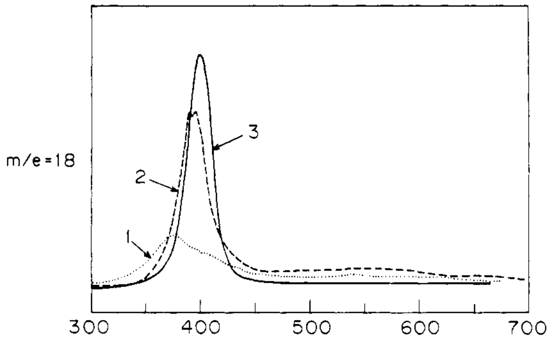

Figure 4. Water desorption features following adsorption of (1) 2-methyl-2-propanol, (2) 2-propen-1-ol, and (3) 2-propanol. The zeolite sample size and mass spectrometer sensitivity varied slightly for each curve so that the area under the curves will differ slightly from the actual amount of water leaving the sample.

The calculated energy for the carbenium ion for 2-propen-1-ol is similar to that for 2-propanol, and dehydration again occurs in preference to simple desorption of the alcohol. The temperature at which dehydration occurs for these two alcohols is also very similar. This is shown in Figure 4, where the water desorption features for 2-propen-1-ol and 2-propanol have been plotted together, along with results for 2-methyl-2-propanol for comparison. While 2-propen-1-ol appears to dehydrate at a slightly lower temperature than 2-propanol, the reaction temperature is clearly very similar. Therefore, both the calculations and experiments support the idea that these alcohols exhibit similar reactivities. The results for 2-methyl-2-propanol are clearly different. The $m/e = 18$ feature for this alcohol occurs at the lowest temperature and has the lowest area under the curve. In this case, reaction occurs at room temperature and most of the water has been removed during evacuation.

In spite of the utility of the thermochemical model based on carbenium ion intermediates, the spectral evidence indicates that the stable form of the dehydrated species at the acid site is probably not a true carbenium ion but rather an alkyl silyl ether. However, the fact that the reactivities of the various alcohols vary with their respective carbenium ion stabilities implies that reactivity is still controlled by the accessibility of the carbenium ion from the bound ether.

An additional interesting feature to our experimental results is that the hydrocarbon products formed in desorption of 2-propen-1-ol are mainly simple olefins, like propene, and aromatics rather than allene or other conjugated dienes. Allene and conjugated dienes must be so reactive in the zeolite that hydride transfer and oligomerization reactions occur before these molecules can diffuse out of the zeolite, even for the low pressures at which our experiments were carried out. While it is probably not possible to try to sort out the various secondary reactions that must be taking place in the zeolite, these results show that allylic intermediates like those formed by the adsorption of 2-propen-1-ol can be involved in the formation of aromatics and may well play a role in the chemistry of other small molecules.

Summary

For the adsorption of 2-propen-1-ol in H-ZSM-5, 1:1 adsorption complexes with the framework Al can be easily identified. These complexes dehydrate above 400 K to form an allylic intermediate, which then undergoes secondary reactions to form a range of olefin and aromatic products. Spectroscopic evidence suggests that the allylic intermediate is likely to be an alkyl silyl ether. However, the ease of forming dehydration products from the 1:1 adsorption complex with 2-propen-1-ol compared to that for other alcohols is well described by the relative gas-phase stability of the allylic carbenium ion, implying that formation of the carbenium ion must be an important step in the reaction sequence.

Registry No. 2-Propen-1-ol, 107-18-6.