

Stoichiometric Adsorption Complexes in H-ZSM-5

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We have examined the adsorption of methanol, 2-propanol, and 2-methyl-2-propanol on H-ZSM-5 samples with silica/alumina ratios of 38, 70, and 520 using temperature-programmed desorption (TPD) and thermogravimetric analysis (TGA) to examine the effect of Al concentration on the strength of the acid sites. In agreement with the results of a previous study [M. T. Aronson, R. J. Gorte, and W. E. Farneth, *J. Catal.* **98**, 434 (1986)], a clearly defined adsorption state corresponding to a coverage of one molecule per Al atom could be identified for each of the alcohols on each of the zeolites, with the possible exception of methanol on H-ZSM-5(520). Furthermore, the unimolecular reactivities of the molecules in these 1 : 1 adsorption complexes are unaffected by the Al concentration. Only secondary reactions, such as the extent of the oligomerization of olefin products formed from 2-propanol and 2-methyl-2-propanol, are found to be different for the different samples. Adsorption complexes with a 1 : 1 stoichiometry are also observed following adsorption and evacuation of 2-propanamine and 2-propanone on several zeolite samples, showing that molecules with other functional groups also form adsorption complexes at the Al sites. These results imply that the acid sites in H-ZSM-5 are identical and are present at a concentration of one per Al atom. © 1988 Academic Press, Inc.

INTRODUCTION

To better understand the acidic properties of H-ZSM-5, we have been investigating the chemisorption of simple adsorbates which can undergo classical acid-catalyzed chemistry, such as alcohols which can undergo dehydration (1-4) and toluene which can participate in H/D exchange (5). An important discovery in this work was that a well-defined adsorption state corresponding to one molecule per Al site can be observed for toluene and most of the simple alcohols. The trends observed in these adsorption experiments implied that proton transfer from the hydroxyls at the Al sites to the adsorbed molecules plays an important role in adsorption (3). Furthermore, the reactivities of the molecules associated with the 1 : 1 adsorption complex are consistent with all of the Al sites having identical acid strengths.

In our previous work, all of the zeolite samples had a SiO₂/Al₂O₃ ratio of approxi-

mately 70. While the linear dependence between *n*-hexane cracking rates and Al content in H-ZSM-5 samples that have been pretreated under mild conditions (i.e., in the absence of steam) suggests that Al concentration does not affect the strength of the acid sites in H-ZSM-5 (6), the acid strengths of other zeolites have been shown to be strongly dependent on Al content (7, 8). Therefore, to check the effect of Al concentration on the acid sites in H-ZSM-5, we have extended our previous investigations by examining the adsorption of methanol, 2-propanol, and 2-methyl-2-propanol on H-ZSM-5 samples with SiO₂/Al₂O₃ ratios of 38 and 520. The three alcohols that we studied were chosen because they showed large differences in their reactivities for the 1 : 1 adsorption complex during temperature-programmed desorption (TPD) (3). In this paper, we will show that a clearly defined state corresponding to one molecule per Al atom is found for each of these alcohols on H-ZSM-5, independent of SiO₂/Al₂O₃ ratio,

with the possible exception of methanol on H-ZSM-5(520). Furthermore, the unimolecular reactivities of the 1:1 adsorption complexes for dehydration, as measured by TPD, are also found to be independent of the Al concentration. Finally, we will show that a 1:1 adsorption complex can also be observed for compounds with other chemical groups such as amines and ketones. All of our results imply that carefully prepared H-ZSM-5 consists of identical, noninteracting sites associated with the tetrahedral Al atoms in the zeolite framework.

EXPERIMENTAL TECHNIQUES

The equipment and procedures used to measure adsorption in these studies were very similar to those used previously (1-5). TPD and thermogravimetric analysis (TGA) experiments were carried out simultaneously using a Cahn 2000 microbalance mounted within a high vacuum chamber. The system was evacuated with a turbomolecular pump and had a base pressure below 1×10^{-7} Torr. The sample weight could be continuously measured using the microbalance, and desorption was carried out *in vacuo* so that the desorbing species could be directly observed using a Spectramass mass spectrometer. This spectrometer was interfaced with a microcomputer to allow several mass peaks to be monitored simultaneously during a TPD experiment. A thermocouple placed near the sample was used for temperature measurement, and the heating rate during desorption was maintained at 10 K/min by a feedback controller. The samples consisted of between 13 and 27 mg of zeolite spread over a flat pan to avoid bed effects (9).

The zeolites were exposed to the various adsorbates at 295 K by admitting the vapors from a liquid sample into the vacuum chamber until no further uptake could be measured by the microbalance. We did not make any effort to control the pressure of the various adsorbates since, in the pressure range we were working, a substantial fraction of the zeolite pore volume was

TABLE 1
Saturation Gravimetric Uptakes for Each Adsorbate in H-ZSM-5 at 295 K

Adsorbate	g/100 g zeolite	Fraction pore ^a volume filled
Methanol	9.9	0.66
2-Propanol	12.7	0.85
2-Methyl-2-propanol	10.8	0.73
2-Propanamine	11.5	0.88
2-Propanone	12.3	0.82

Note. The values shown are the averages of those found for the different zeolites.

^a Assumes that each adsorbate packed at its liquid density into the zeolite and that the porosity of the ZSM-5 is 0.19 cm³/g.

filled with each of the adsorbates, making the saturation coverage only weakly dependent on pressure. The saturation coverages for each of the molecules were found to be approximately independent of the SiO₂/Al₂O₃ ratio of the sample and did not differ by more than 8% from the average values given in Table 1 for any of the zeolites studied. Following saturation of the samples by the adsorbate, the system was evacuated for varying lengths of time to remove weakly adsorbed molecules.

To identify the products that were formed during the TPD experiment, the mass range 10-70 *m/e* was examined at 15-K intervals. The desorption experiments were then repeated using the computer to monitor the mass peaks which could be used to identify each product. The particular *m/e* ratios used for each of the products are shown in Table 2. Over the course of an experimental sequence involving one adsorption/desorption cycle, the total mass change in the zeolite was found to be negligible for each of the molecules examined, with the exception of methanol on a sample with a SiO₂/Al₂O₃ ratio of 520, indicating that no residual products were left undetected in the zeolite.

Zeolite samples with SiO₂/Al₂O₃ ratios of 38, 70, and 520 were obtained as NH₄-ZSM-

TABLE 2
Values of m/e in the Mass Spectra
Which Were Used to Monitor
Desorbing Products

Product	m/e
Water	18
Ammonia	17
Methanol	31
2-Propanol	45
2-Methyl-2-propanol	59
Propene	41
Butenes	41, 55
Olefins larger than butene	41, 69
2-Propanamine	44
2-Propanone	43

5 powders from the Mobil Oil Company and are designated as ZSM-5(38), ZSM-5(70), and ZSM-5(520) in this paper. Electron microscopy indicated that the particles of ZSM-5(70) and ZSM-5(520) were uniformly between 0.4 and 0.5 μm in diameter and that the particles of ZSM-5(38) were uniformly between 0.9 and 1.0 μm in diameter. X-ray diffraction of these samples agreed with the published data for ZSM-5(10). The Al content was checked using ^{27}Al NMR of the hydrated samples, with an aqueous solution of $\text{Al}(\text{NO}_3)_3$ as a reference (11). While only tetrahedral Al was observed in the samples of ZSM-5(70) and ZSM-5(520), a small amount (5–10%) of octahedral aluminum was detected in the samples of ZSM-5(38). The results of the calibration, listed in Table 3, show that the measured Al concentrations agreed with those reported to us by Mobil within 10%. Due to uncertainties in the ^{27}Al NMR technique (12), we

TABLE 3
Measured Silica/Alumina Ratios for the H-ZSM-5
Samples Used in the TPD-TGA Experiments

Sample	Reported by Mobil	From ^{27}Al NMR
H-ZSM-5(38)	38	35
H-ZSM-5(70)	70	62
H-ZSM-5(520)	520	470

used the Al concentrations reported to us by Mobil to calculate adsorption stoichiometries. For all of the experiments reported in this paper, the hydrogen form of the zeolite was prepared by heating $\text{NH}_4\text{-ZSM-5}$ to 700 K *in vacuo*.

RESULTS

We have previously reported the TPD-TGA results for simple alcohols on a H-ZSM-5 sample with a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 70 (3). In work presented in this paper, only methanol, 2-propanol, and 2-methyl-2-propanol were examined since they each showed a clearly defined adsorption state corresponding to a coverage of one molecule/Al site, with significant differences in reactivity during desorption of this 1:1 complex. Methanol was completely unreactive in desorption; 2-propanol reacted completely to propene and water but only after heating to above 360 K; and 2-methyl-2-propanol reacted completely at room temperature, with the water formed by dehydration desorbing during the evacuation period at 295 K. In the present study, these same trends emerge, independent of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. To determine the effect of the functional group on adsorption, we have also examined the adsorption of 2-propanamine and 2-propanone. The results for each of the different molecules will be discussed individually.

In all of our adsorption experiments, the samples were initially saturated with the compound of interest so that a substantial fraction of the pore volume was filled with the adsorbate molecules, followed by a period of evacuation. Table 4 shows the adsorbate coverages after evacuation for 60 min and after longer times. For most of the adsorbates examined, between one and two molecules per Al site remained in the zeolite after prolonged evacuation, regardless of Al content, the exception being 2-propanamine. Not surprisingly, evacuation to coverage of one molecule per Al required much longer times for the H-ZSM-5(520) sample. Assuming that the absolute coverage of weakly adsorbed molecules will de-

TABLE 4

Coverages following Evacuation for Each of the Different Adsorbates on Each of the Zeolite Samples

Adsorbate	SiO ₂ /Al ₂ O ₃	Following 60 min of evacuation		Following prolonged evacuation	
		g/100 g	molecules/Al	g/100 g	molecules/Al
Methanol	38	2.2	0.85	2.1	0.82
	70	—	—	1.5	1.0
	520	0.4	1.9	0.4	1.9
2-Propanol	38	5.3	1.0	4.9	0.93
	70	—	—	4.6	1.0
	520	1.6	4.0	0.89	2.3
2-Methyl-2-propanol	38	6.4	1.3	5.6	1.1
	70	—	—	3.5	1.0
	520	0.69	2.0	0.49	1.3
2-Propanamine	70	5.7	2.1	4.9	1.8
	520	2.1 ^a	5.5 ^a	1.4	3.8
	2-Propanone	70	2.7	1.0	2.6

^a Following 30 min of evacuation.

cline exponentially with time, it is reasonable that evacuation times would need to be almost ten times longer on the H-ZSM-5(520) sample to reach the one molecule per Al value. While the absolute coverages for each of the adsorbates on H-ZSM-5(520) following evacuation were always much lower than those on the samples with higher Al concentrations, coverages expressed in terms of molecules per Al site were much more sensitive to small amounts of weak adsorption. The fact that this additional adsorption is due to weakly adsorbed species for most of the molecules studied, and not to additional strong adsorption states, will become more apparent in our discussion of the TPD results.

Alcohol Adsorption

The TPD-TGA results for methanol on H-ZSM-5(38) and H-ZSM-5(520) are shown in Fig. 1; the results for H-ZSM-5(70) have been published previously (1, 3). TPD measurements on all three zeolites showed mainly methanol ($m/e = 31$) desorbing from the samples in a peak centered at approximately 400 K. Some dimethyl ether ($m/e = 45$) was also observed at higher tempera-

tures on the samples with silica/alumina ratios of 38 and 70. Since methanol does not evacuate easily in ultrahigh vacuum, we believe this dimethyl ether is formed by the reaction of background gases over the zeolite at high temperatures during TPD and is not the result of a different type of adsorbed methanol. The formation of a 1:1 methanol adsorption complex was easily observed on the H-ZSM-5(38) and H-ZSM-5(70) samples. On H-ZSM-5(70), evacuation down to a coverage of one molecule per site occurred fairly rapidly at room temperature, while evacuation to lower coverages was not possible in reasonable times (3). Also, TPD curves measured after short evacuation times in which the initial methanol coverage corresponded to more than one molecule per Al site exhibited an additional low-temperature feature (1). The results were very similar on the H-ZSM-5(38) sample, except that the coverage of the strongly adsorbed methanol was only 0.8 molecule/Al. Since a stoichiometry of approximately 0.8/Al was also observed for strongly bound 2-propanol on this sample, this probably indicates that some of the Al atoms in this sample are not associated with acid sites,

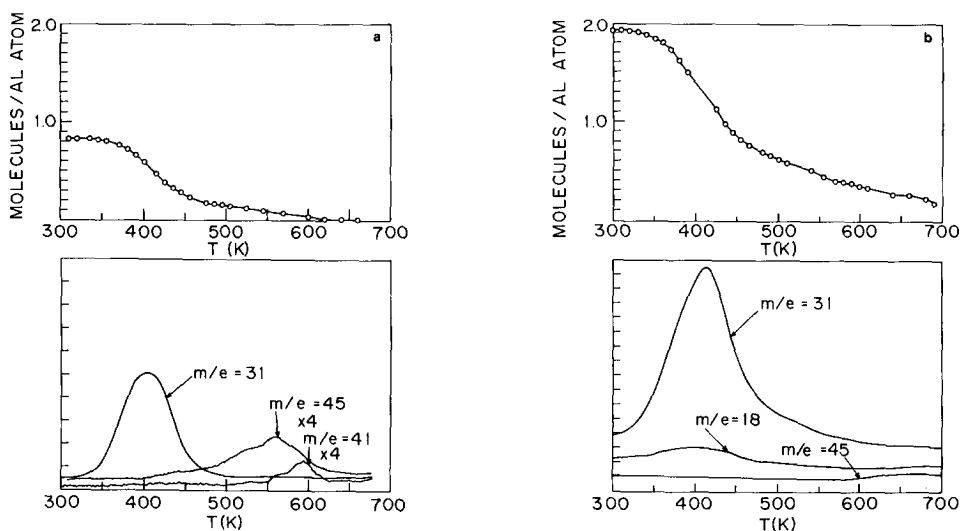


FIG. 1. (a) TPD and TGA results for methanol on H-ZSM-5(38). Most of the methanol ($m/e = 31$) desorbed unreacted; however, some secondary products (dimethyl ether, $m/e = 45$) were observed at higher temperatures. (b) TPD and TGA results for methanol on H-ZSM-5(520). The residual weight change in the sample following the temperature ramp is believed to be due to methoxylation of silanol groups in the zeolite.

either due to incomplete exchange of the cations or to some of the Al atoms being outside the zeolite framework. Indeed, the ^{27}Al NMR results in Table 2 suggest the presence of nonframework Al in the H-ZSM-5(38) sample.

An additional aspect of methanol adsorption became apparent on the H-ZSM-5(520) sample. In terms of absolute methanol coverages, the amount remaining in the zeolite during evacuation on this sample was always much less than was found on the zeolites with higher Al concentrations. However, in terms of molecules per Al site, we were able to evacuate only to a coverage of 1 molecule/Al after prolonged evacuation (~ 50 h). We also found that, following evacuation to a coverage corresponding to between one and two molecules per Al, not all of the methanol that was adsorbed in excess of the 1:1 ratio could be removed easily during TPD. While the majority of the methanol ($m/e = 31$) on this sample desorbed in a peak centered at approximately 400 K, a coverage corresponding to between 0.15 and 0.3 molecule/Al would not

easily desorb even at 700 K *in vacuo*. The zeolite sample weight could be returned to its original value following the adsorption and subsequent desorption of methanol only by prolonged evacuation at temperatures above 700 K or by heating the sample in O_2 . We tentatively attribute this small quantity of methanol which remained in the zeolite to high temperatures as being due to methoxylation of silanol groups (13).

The formation of a 1:1 adsorption complex was observed more easily with 2-propanol. In previous TPD-TGA measurements on H-ZSM-5(70), we found that it was possible to evacuate the saturated sample to a 1/Al coverage and that all of the 2-propanol in this 1:1 complex desorbed as propene and water at 400 and 405 K, respectively (3). When shorter evacuation times or poorer evacuation techniques were used so that the initial coverage of 2-propanol was greater than 1/Al, the excess 2-propanol desorbed unreacted below 360 K (2). The results for the other two zeolite samples were virtually identical, as shown in Fig. 2. In TPD curves for H-ZSM-5(520)

with an initial coverage of 2.3 molecules/Al, shown in Fig. 2b), more than half of the alcohol desorbed unreacted below 400 K. The remaining 2-propanol, at a coverage corresponding to approximately 1/Al, desorbed as water ($m/e = 18$) and propene ($m/e = 41$) between 400 and 450 K. The sample weight returned to its initial value following the TPD experiment. While the desorption features for all species on this sample occurred at slightly higher temperatures and were somewhat broader than was found on H-ZSM-5(70), this is probably related to the experimental conditions and not a reflection of the strength of the acid sites since desorption features can be strongly influenced by transport properties and experimental conditions (9). Since the reactivities of the 1:1 species to form propene and water on both zeolite samples were so similar, we conclude that the 2-propanol molecules associated with this complex are essentially identical.

The results for 2-propanol on H-ZSM-5(38), shown in Fig. 2a, reinforce this conclusion. Just as we observed with methanol

adsorption on this sample, we were able to evacuate 2-propanol below the coverage expected for the 1:1 adsorption complex; and the amount of 2-propanol that reacted to water and olefin products during TPD corresponded to approximately 0.8 molecule/Al. Therefore, results for both methanol and 2-propanol on the H-ZSM-5(38) sample are consistent with a fraction of the Al not being associated with acid sites. The remaining 2-propanol molecules which are associated with acidic Al sites react completely to form dehydration products above 400 K, in the same temperature range observed on both of the other samples.

The new feature in the TPD results for 2-propanol on H-ZSM-5(38), not observed with the other two zeolite samples, is the formation of higher molecular weight olefin products, as evidenced by the peak at $m/e = 55$ in the mass spectrum of the desorbing products. Since butenes and larger olefins have major peaks at both $m/e = 41$ and $m/e = 55$ in their cracking patterns while propene would not exhibit a peak at $m/e = 55$, the olefins desorbing above 420

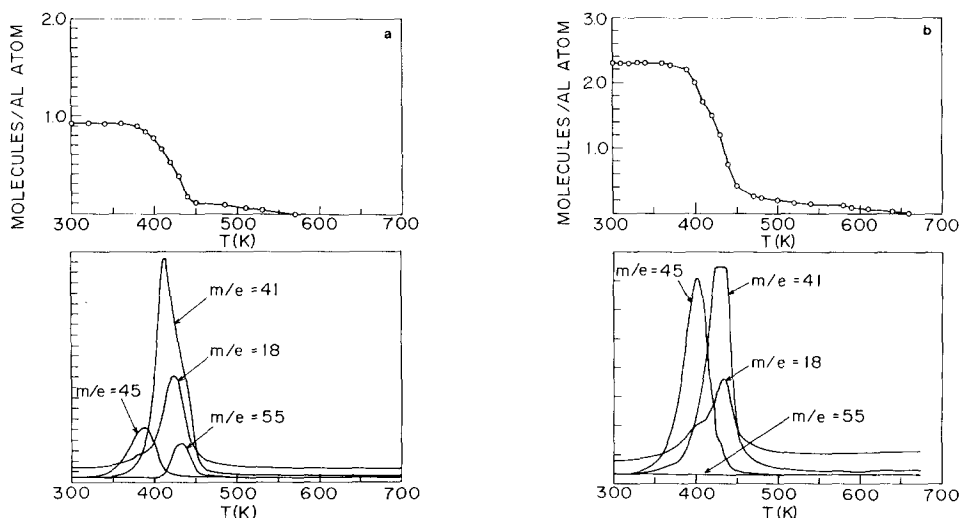


FIG. 2. TPD and TGA results for 2-propanol on (a) H-ZSM-5(38) and (b) H-ZSM-5(520). On both samples, a complex corresponding to a coverage close to 1 molecule/Al can be identified in the TPD curves which desorbs as propene ($m/e = 41$) and water ($m/e = 18$). 2-Propanol ($m/e = 45$) adsorbed in excess of 1/Al desorbed unreacted at lower temperatures. Some oligomerization of the desorbing propene also occurred on H-ZSM-5(38), as shown by the presence of a peak at $m/e = 55$ in the mass spectrum of the desorbing products.

K (in Fig. 2a) have undergone secondary reactions. Only propene was observed during the desorption of 2-propanol from the samples with lower Al concentrations. Since propene oligomerization occurs rapidly on H-ZSM-5 upon propene adsorption, even at room temperature (2), the observation of bimolecular chemistry on the H-ZSM-5(38) sample must be due to the higher intrazeolite concentrations of propene during desorption. The dependence on acid site density of the extent of secondary oligomerization chemistry during TPD was also observed in the experiments with 2-methyl-2-propanol.

While oligomerization chemistry and the effect of acid-site concentration on secondary reactions in TPD become more pronounced for 2-methyl-2-propanol, the concept of identical acid sites in a concentration of 1/Al atom, with a unimolecular activity for alcohol dehydration independent of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio, still applies. On H-ZSM-5(70), the weight change following exposure to the alcohol for 5 min and then evacuation corresponds to slightly less than one butene molecule per Al (3, 4). During TPD, mainly olefin products larger than butenes were observed leaving the sample, with no unreacted alcohol and only a small amount of water being observed. As discussed in previous papers, this implies that 2-methyl-2-propanol reacts on the acid sites at room temperature and that the water produced by dehydration is removed during evacuation along with the alcohol in excess of 1/Al.

The results for adsorption of 2-methyl-2-propanol on H-ZSM-5(38) are shown in Fig. 3 and are identical to those on H-ZSM-5(70) with the exception that the initial coverage following evacuation is slightly greater than 1/Al. Again, no unreacted alcohol and only a small amount of water are observed in TPD. Some of the olefins ($m/e = 41$) desorbing from the sample have a higher molecular weight than butene, as evidenced by the peak at $m/e = 69$ in the cracking pattern of the products in the mass spectrum. The

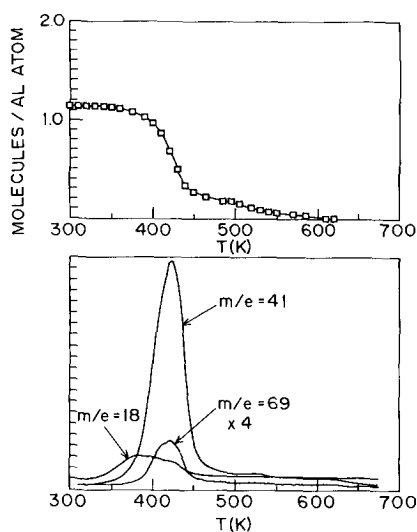


FIG. 3. TPD and TGA results for 2-methyl-2-propanol on H-ZSM-5(38). No unreacted alcohol ($m/e = 59$) and only a small amount of water ($m/e = 18$) are observed in TPD. Some of the olefins ($m/e = 41$) desorbing from the sample in a peak centered at 420 K have a higher molecular weight than butene, as shown by the peak at $m/e = 69$ in the cracking pattern of the products.

observation of a coverage above 1/Al on this zeolite, even though the results for methanol and 2-propanol suggest that only 80% of the Al atoms are associated with acid sites, is probably due to oligomerization which occurs during exposure of the zeolite to the gas-phase alcohol. It has been shown that prolonged exposures (~ 1 – 20 h) of H-ZSM-5(70) to 2-methyl-2-propanol vapor at 295 K can lead to very large oligomer chains (11). This secondary chemistry appears to occur more easily on H-ZSM-5(38) compared to H-ZSM-5(70) for similar exposures to 2-methyl-2-propanol. This is probably related to increased oligomerization rates with increased adsorbate concentrations and acid-site densities.

The results with 2-methyl-2-propanol on H-ZSM-5(520) are also consistent with the alcohol reacting rapidly on the acid sites at room temperature; however, the extent of oligomerization of the olefin products is lower due to the lower acid site density. This is completely analogous to our results

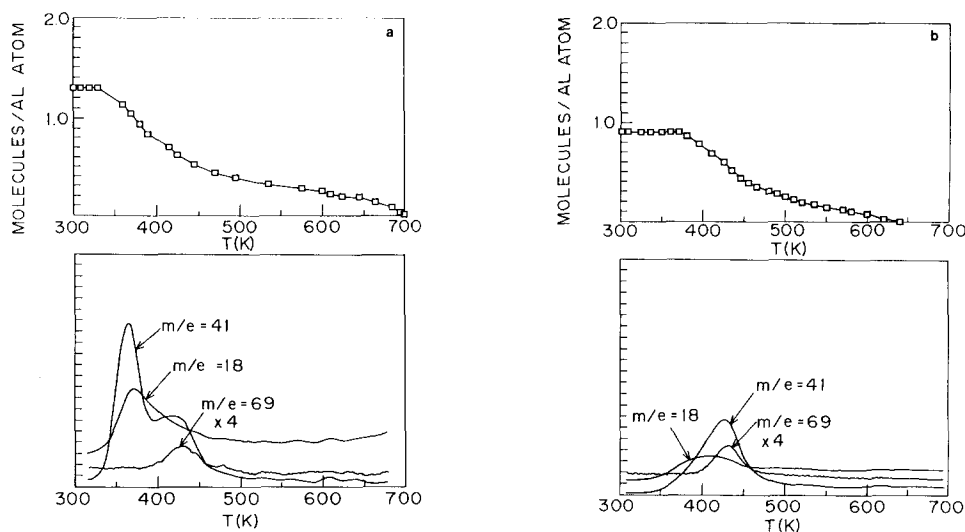


FIG. 4. TPD and TGA results obtained for 2-methyl-2-propanol on H-ZSM-5(520) following evacuation for (a) 5 h and (b) 20 h. No unreacted alcohol ($m/e = 45$) was observed in either case and the water peak ($m/e = 18$) was smaller than that which would be expected for a coverage of 1/Al. The olefin products were monitored using $m/e = 41$ and $m/e = 69$. The observation of a peak at $m/e = 69$ shows that the olefins desorbing in the TPD feature centered at 420 K are due to olefins larger than butenes.

for 2-propanol, where oligomerization during TPD was not important for the zeolites with higher silica-alumina ratios. The TPD curve obtained following exposure to the alcohol and then evacuation for 3 h is shown in Fig. 4a. No unreacted alcohol desorbs from the sample, but the olefin products monitored using the $m/e = 41$ peak now show two maxima centered at 360 and 420 K. Using the fact that higher-molecular-weight olefins exhibit an additional peak at $m/e = 69$ in their mass spectrum, the maximum at 360 K in the $m/e = 41$ curve can be identified as butene, while the maximum at 420 K is due to larger olefins. The TPD results also demonstrate the mobility of butene in the zeolite at room temperature and give further indication of how oligomerization can occur. Figure 4b shows the TPD results on this same sample with the only difference being that evacuation was carried out for 20 h prior to beginning the TPD measurement. After this longer evacuation period, only higher-molecular-weight olefins are observed desorbing from the sample. The intermediate formed by the de-

composition of 2-methyl-2-propanol either was removed from the sample as butenes by evacuation or migrated to adjacent sites to form larger olefins which remained in the zeolite to higher temperatures.

2-Propanamine and 2-Propanone

The TPD-TGA results for 2-propanamine on H-ZSM-5(70) and H-ZSM-5(520) are shown in Figs. 5a and b, respectively. After saturation exposures, we were unable to evacuate to a coverage of 1/Al site in reasonable times on either zeolite. Following 7–13 h evacuation, the coverage on H-ZSM-5(70) corresponded to 2 molecules/Al and the coverage on H-ZSM-5(520) corresponded to almost 4/Al. However, during TPD, additional 2-propanamine above the 1:1 coverage desorbed unreacted ($m/e = 44$) in a broad feature below 500 K, leaving a clearly defined adsorption state corresponding to a 1:1 stoichiometry with the Al sites. We interpret this result as indicating that the molecules adsorbed in excess of the stoichiometric quantity are more weakly adsorbed

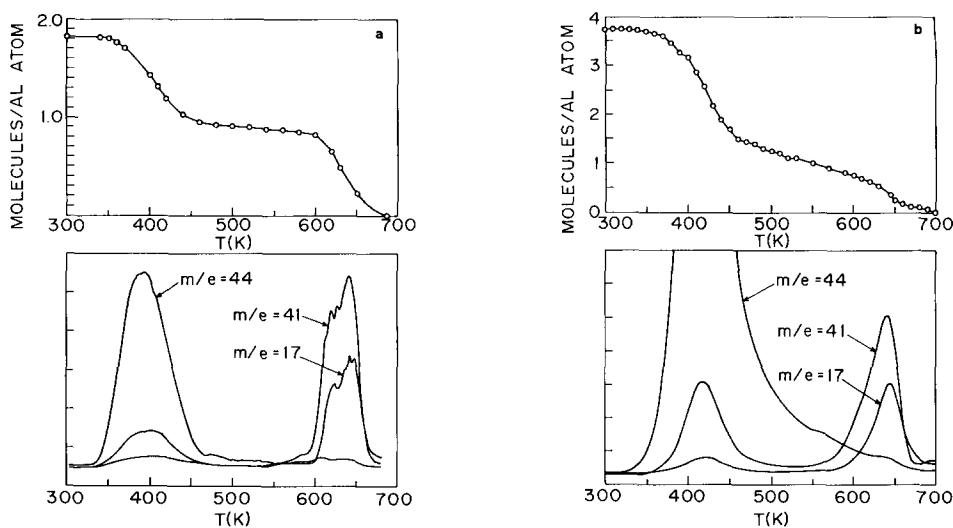


FIG. 5. TPD and TGA results for 2-propanamine on (a) H-ZSM-5(70) and (b) H-ZSM-5(520). On both zeolite samples, a desorption state corresponding to a coverage of 1/Al can be identified which desorbs as propene ($m/e = 41$) and ammonia ($m/e = 17$) between 600 and 650 K. 2-Propanamine adsorbed at a coverage above 1/Al desorbed unreacted ($m/e = 44$) below 500 K. The multiple peaks in the high-temperature feature of (a) are due to oscillations in the heating rate at this temperature.

and are not associated with acid sites. Weakly adsorbed 2-propanamine is more strongly bound to the zeolite channels than were the alcohols, but the presence of these molecules does not imply weak acid sites.

The 1:1 adsorption complex which remains on the surface when the sample is heated above 500 K appears to be well described as an isopropyl ammonium ion and its chemistry is unaffected by Al concentration. First, infrared spectroscopy shows that the hydroxyl peak at 3605 cm^{-1} , which has been associated with the Al sites in H-ZSM-5 (14, 15), is not present following adsorption of the amine and heating to above 500 K *in vacuo*. Furthermore, on both zeolites examined, this 1:1 adsorption complex reacts in TPD to desorb simultaneously as propene ($m/e = 41$) and ammonia ($m/e = 17$) between 600 and 650 K. This chemistry is well known for quarternary ammonium hydroxides in solution where it is the last step of the Hofmann degradation sequence. This temperature range is well above the desorption temperatures for either propene (peak temperature

of 400 K in TPD of 2-propanol) or ammonia ($\sim 500\text{ K}$ under the conditions of our experiment), implying that the simultaneous desorption feature is a measure of the decomposition reaction. Again, the temperature at which the reaction to form propene and ammonia occurs is the same on both zeolites, implying that the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio does not affect the molecules in the adsorption complex.

As a final test of the idea that proton transfer plays an important role in adsorption on H-ZSM-5, we measured the TPD-TGA curves for 2-propanone on H-ZSM-5(70), with the results shown in Fig. 6. The gas-phase, proton affinity for 2-propanone is 197 kcal/g mol , which is considerably higher than that of 2-propanol (193 kcal/g mol) (16). While no acid-catalyzed chemistry should occur with 2-propanone, a 1:1 complex should be expected to form if proton transfer is important and the 1:1 complex should have a stability similar to that found for the simple alcohols. Its stability should also be considerably higher than that found for simple alkanes which can be eas-

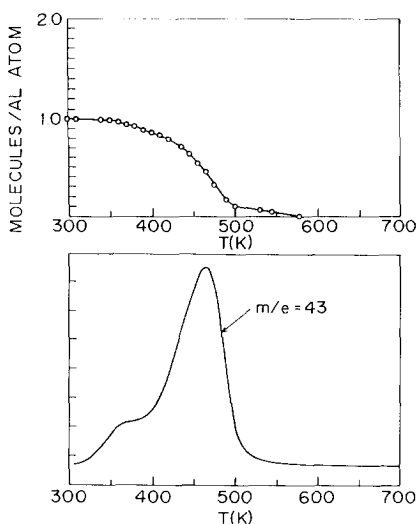


FIG. 6. TPD and TGA results for 2-propanone on H-ZSM-5(70). 2-Propanone can be evacuated to a coverage of 1/Al at 295 K, with the remaining 2-propanone ($m/e = 43$) desorbing unreacted in a broad feature centered at 465 K.

ily evacuated in our apparatus. As expected, the results show that 2-propanone can be evacuated to a coverage of 1/Al at room temperature, with the remaining 2-propanone desorbing unreacted in a broad feature centered at 465 K. Infrared spectra of the sample following adsorption and evacuation again provided evidence that the 2-propanone molecules were associated with the Al hydroxyls since the peak at 3605 cm^{-1} was completely removed.

DISCUSSION

The TPD-TGA results discussed in this paper show that the 1:1 adsorption stoichiometry observed between the simple alcohols and the Al sites in previous studies on H-ZSM-5(70) can also be observed with zeolites having other Al concentrations and with molecules having other functional groups. While each of the molecules substantially filled the pore volume on each of the zeolites under saturation conditions, a separate, more strongly bound state with a coverage corresponding to a 1:1 stoichiometry could be identified in most cases. The only exception to this was observed with

methanol on H-ZSM-5(520), where a small amount of methanol could not be easily removed by heating. Since strongly bound states above the 1:1 stoichiometry were not observed for any of the other adsorbates and since methoxylation of silanol groups has been observed previously on silica (13), we do not believe that this additional, strongly bound methanol necessarily represents new acid sites.

Furthermore, the unimolecular reactivity of the entire series of 1:1 adsorption complexes was unaffected by the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. On each of the three zeolite samples, 2-methyl-2-propanol complexes at the Al sites reacted completely at 295 K, 2-propanol reacted completely to olefin products and water at higher temperatures, 2-propanamine reacted to propene and ammonia between 600 and 650 K, and methanol and 2-propanone desorbed unreacted. While differences in the extent of secondary reactions, like the formation of olefin oligomers from 2-methyl-2-propanol, were observed with changes in the Al concentration, these effects are almost certainly due to the concentrational dependence of bimolecular reactions and not to any differences in the strength of the acid sites.

Our results imply that a dilute concentration of tetrahedral Al atoms in a ZSM-5 lattice leads to identical acid sites in a concentration of 1/Al; i.e., the zeolite can be thought of as a collection of identical, independent sites located near tetrahedral Al atoms. This is in agreement with *n*-hexane cracking results on both H-ZSM-5 and dealuminated Y zeolites, where it has been shown that the activity increases linearly with the Al content for carefully prepared samples (6, 17). Furthermore, the specific activities for hexane cracking carried out under the same reaction conditions over dealuminated Y and H-ZSM-5 zeolites with the same silica/alumina ratio were virtually identical, implying that the specific activity of the acid sites is independent of the zeolite structure (18).

It should be noted that the conclusions

we have reached do not extend to zeolites with low silica/alumina ratios or to materials that have been steamed. It has long been known that the acidity of faujasites is a function of silica/alumina ratio; however, these measurements are usually performed on samples with silica/alumina ratios below 10. In a study of acid-catalyzed reactions on dealuminated Y zeolites, it was shown that the linear relationship between activity and the number of Al atoms present in the zeolite unit cell was not valid above 35 Al/unit cell ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 9$), implying that other factors must be important at higher Al concentrations (19). In the case of zeolites that have been steamed, changes can be observed both in the ^{27}Al NMR spectra (20, 21) of the zeolite and in the hydrocarbon cracking activity (6) following high temperature steaming. High temperature steaming appears to generate a new type of acid site by making structural changes in the zeolite. In the work which we have discussed in this paper, we have attempted to avoid pretreatment conditions that could lead to these complications.

The ideal, dilute sites in our samples have Brønsted character since the 1:1 adsorption complexes observed in this study involve proton transfer between the Al hydroxyls and the adsorbate molecules. Evidence for the importance of proton transfer to alcohols to form oxonium ion-like species has been discussed elsewhere (3, 4). In the case of the intermediates formed from alcohol dehydration, ^{13}C NMR spectra of adsorbed $(\text{CH}_3)_3^{13}\text{COH}$ have shown that the dehydrated intermediate can best be thought of as an alkyl-silyl ether in which the t-butyl alkyl group is covalently bonded to the oxygen of the zeolite framework (14). This ether species can form a gas-phase olefin by transfer of a proton from the alkyl group back to the zeolite, indicating again that proton transfer is important in the adsorption process. Evidence for the importance of proton transfer in the adsorption of 2-propanamine and 2-propanone has been discussed earlier in this paper.

While the acid sites in nonsteamed H-ZSM-5 may be identical and unaffected by concentration, other factors may influence the observed chemistry in high-pressure, high-temperature reaction environments. Our methods are designed to promote unimolecular chemistry, but even under these conditions bimolecular chemistry is very important in certain cases (3). Since $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios will affect the adsorbate concentration, one should expect to observe apparent reactivity changes due to the effects of this concentration. These reactivity changes do not, however, affect the conclusions we have reached concerning the chemical properties of an individual site.

SUMMARY

We have demonstrated that adsorption complexes with a coverage of one molecule per Al atom can be formed with a series of simple alcohols and with 2-propanamine and 2-propanone in H-ZSM-5. Proton transfer from the zeolite hydroxyls associated with the Al sites to the adsorbates appears to play an important role in forming these adsorption complexes. Furthermore, the reactivity of these stoichiometric complexes is unaffected by changing the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the zeolite from 38 to 520. These results imply that carefully prepared H-ZSM-5 consists of identical Brønsted acid sites in a concentration equal to the concentration of tetrahedral Al atoms in the zeolite framework.

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