# Stoichiometric Adsorption Complexes in H-ZSM-5, H-ZSM-12, and H-Mordenite Zeolites[1]

## INTRODUCTION

In order to understand the chemical properties of acid sites in zeolites, we have been examining the adsorption of simple molecules which can undergo classical acid-catalyzed chemistry in high-silica H-ZSM-5 (1–8). For many molecules, including a series of alcohols, toluene, 2-propanamine, and 2-propanone, we have found that, following adsorption and evacuation, a well-defined adsorption complex corresponding to one molecule per Al site could be obtained. Furthermore, the unimolecular reactivities of the molecules in these 1 : 1 adsorption complexes were consistent with solution-phase, Brønsted acid-catalyzed chemistry and were unaffected by the Al concentration for $SiO_2/Al_2O_3$ ratios from 38 to 520 (8). These results imply that the active acid sites in H-ZSM-5 are identical and are present in a concentration of one/Al atom. This is consistent with conclusions reached from n-hexane cracking studies on H-ZSM-5 (9).

In order to examine the effect of solid-state structure on these acid sites, we have extended our previous work to two other zeolites, H-ZSM-12 and H-mordenite. H-mordenite and H-ZSM-12 zeolites were chosen for this comparison because they differ significantly in structure from H-ZSM-5, having one-dimensional channels composed of 12-membered rings rather than the two-dimensional channels with 10-membered rings that are present in ZSM-5. In addition, all three zeolites could be prepared with a comparable $SiO_2/Al_2O_3$ ratio so that the effect of zeolite structure could be isolated from effects due to differences in Al concentration. The adsorption of 2-propanol and 2-propanamine were chosen for study since the 1 : 1 complexes formed by these two molecules were the most distinctive in our previous adsorption studies. On each of the H-ZSM-5 samples examined previously, the 1 : 1 complex with 2-propanol was found to desorb as propene and water at just above 400 K and the 1 : 1 complex with 2-propanamine was found to react to propene and ammonia between 600 and 650 K. The 2-propanol and 2-propanamine molecules adsorbed in excess of the 1 : 1 stoichiometry were found to desorb unreacted at lower temperatures under the conditions of our experiment.

We will show in this paper that 2-propanol and 2-propanamine also form clearly defined, 1 : 1 adsorption complexes with the Al site in H-ZSM-12 and H-mordenite. The reactivity of these adsorption complexes is identical to the reactivity of the 1 : 1 adsorption complexes formed by these molecules in H-ZSM-5. The complexes decompose at the same temperatures and form the same products on all three zeolites. This is strong evidence that the acid sites formed by isolated Al atoms in a zeolite lattice are chemically equivalent, independent of the structure of the lattice.

## EXPERIMENTAL TECHNIQUES

The ZSM-5 sample used in this study was obtained as $NH_4$-ZSM-5 powder from the Mobil Oil Company. Both the ZSM-12 and

mordenite samples were synthesized in a hydrothermal system with tetraethyl ammonium bromide as the organic directing agent, aluminum nitrate, sodium hydroxide, silica (Hi-Sil), and water according to procedures described previously (10). The samples were then calcined in air and ammonium ion exchanged. For all of the experiments reported in this paper, the hydrogen form of the zeolite was prepared by heating the ammonium form to 700 K in vacuo. Electron microscopy showed that the ZSM-12 and ZSM-5 samples were uniformly between 0.3 and 0.5 μm in diameter, while the mordenite samples were 0.8 to 1.0 μm in diameter. X-ray diffraction patterns of all the zeolite samples were consistent with the published data (11–13).

The Al concentrations of the different samples were determined using $^{27}$Al NMR of the hydrated zeolites and are shown in Table 1. The ZSM-5 sample was used as a reference to calibrate the NMR intensities since $NH_3$ adsorption measurements on this zeolite sample agreed closely with the $SiO_2/Al_2O_3$ ratio of 70 reported to us by Mobil (1). An aqueous $Al(NO_3)_3$ solution was also used for calibration and gave concentrations which agreed within 10% of those tabulated (14); however, the use of the ZSM-5 as a reference was considered to be more reliable due to uncertainties in the $^{27}$Al NMR technique (15). A small amount of octahedral Al (less than 13% of the total $^{27}$Al NMR signal) was observed on the mordenite sample, but only the signal due to tetrahedral Al was used for calculating Al concentrations in Table 1.

TABLE 1

| Samples | $SiO_2/Al_2O_3$ from $^{27}$Al NMR |
|---|---|
| H-ZSM-5 | 70 |
| H-ZSM-12 | 136 |
| H-mordenite | 79 |

Measured silica–alumina ratios for the zeolite samples used in the TPD–TGA experiments.

The equipment and procedures used to measure adsorption were the same as those used previously (1–5, 7, 8). The temperature-programmed desorption (TPD) and thermogravimetric analysis (TGA) experiments were carried out on a system equipped with a Cahn 2000 microbalance and a quadrupole mass spectrometer. The system could be evacuated with a turbomolecular pump and had a base pressure below $1 \times 10^{-7}$ Torr. Between 13 and 17 mg of zeolite was spread over a flat sample pan of the microbalance to minimize bed effects in adsorption and desorption (16). The TPD and TGA experiments were carried out simultaneously using a heating rate of 10 K/min. During the desorption experiment, the sample weight was continuously monitored using the microbalance and the desorbing species were observed using the mass spectrometer which was interfaced with a microcomputer to allow several mass peaks to be measured simultaneously. A thermocouple placed near the sample was used for temperature measurement.

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 on each of the zeolites examined, indicating that no residual products were left undetected in the zeolite. However, we did observe a linear decrease in weight on each of the clean samples with temperature. This weight change was completely reversible and occurred even at pressures below $1 \times 10^{-7}$ Torr. It was most severe for the mordenite sample, where the apparent weight of the sample at 700 K was approximately 0.5% less than the weight at 300 K and was least important for the H-ZSM-5, where the weight change over this temperature region was only 0.1%. No change was observed when an empty sample pan was placed in the balance. Since the balance was found to be very sensitive to static charges and no evidence for desorbing species could be observed in the mass spectrum when the clean sample was

heated, we believe these apparent changes may be due to static charging. They result in a linear tail which can be seen on each of the TGA curves. The measured weight of the sample at 700 K was used as the reference in each of the experiments.

In all of our adsorption experiments, the samples were initially saturated with the compound of interest by exposing the zeolites to the vapor pressure above the liquid adsorbates at 295 K. While we did not attempt to carefully control the adsorption pressures, a substantial fraction of the zeolite pore volume was filled by each of the adsorbates during this exposure. Table 2 shows the weight uptakes for 2-propanol, n-hexane, and 2-propanamine on each of the different samples, as well as the pore volume which would be filled by liquids with the densities of the adsorbates. Since the porosity of each of the zeolites is approximately 0.2, it is clear that, under the conditions of our experiment, much of the zeolite pore volume is filled in each case. All of the TPD–TGA measurements were obtained following evacuation of the samples for between 3 and 20 h to remove some of the weakly adsorbed material. As we will show, there is a clearly defined adsorption state at a coverage of one/Al atom for each of the adsorbates on each of the zeolites. Variation in evacuation time affected the results only by increasing the amount of weakly adsorbed material at the start of the desorption experiment, but did not otherwise affect the results.

## RESULTS

The TPD–TGA results for 2-propanol on the three different zeolites are shown in Fig. 1. On each of the zeolites, the initial weight change following adsorption and evacuation of 2-propanol corresponded to somewhat more than one molecule/Al atom. While this quantity was dependent on the evacuation time at room temperature, we were never able to evacuate below the one molecule/Al coverage, even after several days evacuation. On the H-ZSM-5 and H-ZSM-12 samples, all 2-propanol adsorbed in excess of one molecule/Al desorbed in TPD as the unreacted alcohol ($m/e = 45$) in a peak between 350 and 400 K. On the mordenite sample, the weight change at the beginning of the experiment corresponded to 1.25 molecules/Al and only a very small amount of unreacted 2-propanol was observed desorbing from the sample below 400 K; however, all sample weights were referenced to that of the clean sample at 700 K. If the linear change observed on heating the clean samples, discussed in the Experimental section, is subtracted from the sample weight, the initial coverage of 2-propanol on the mordenite is very close to one/Al. Therefore, we conclude that the molecules adsorbed in excess of the 1:1 stoichiometry on each of the samples are removed unreacted by evacuation at 295 K or by heating to 400 K and that these molecules are much more weakly bound than those associated with the 1:1 stoichiometry.

TABLE 2

| Sample | 2-Propanol | | 2-Propanamine | | n-Hexane | |
|---|---|---|---|---|---|---|
| | g/100 g | cm³/g[a] | g/100 g | cm³/g[a] | g/100 g | cm³/g[a] |
| H-ZSM-5 | 13 | 0.17 | 11.8 | 0.17 | 12.4 | 0.18 |
| H-ZSM-12 | 9.2 | 0.12 | 9.1 | 0.13 | 7.64 | 0.11 |
| H-mordenite | 7.9 | 0.10 | — | — | 6.3 | 0.09 |

Saturation gravimetric uptakes for each adsorbate on each of the zeolite samples at 295 K.

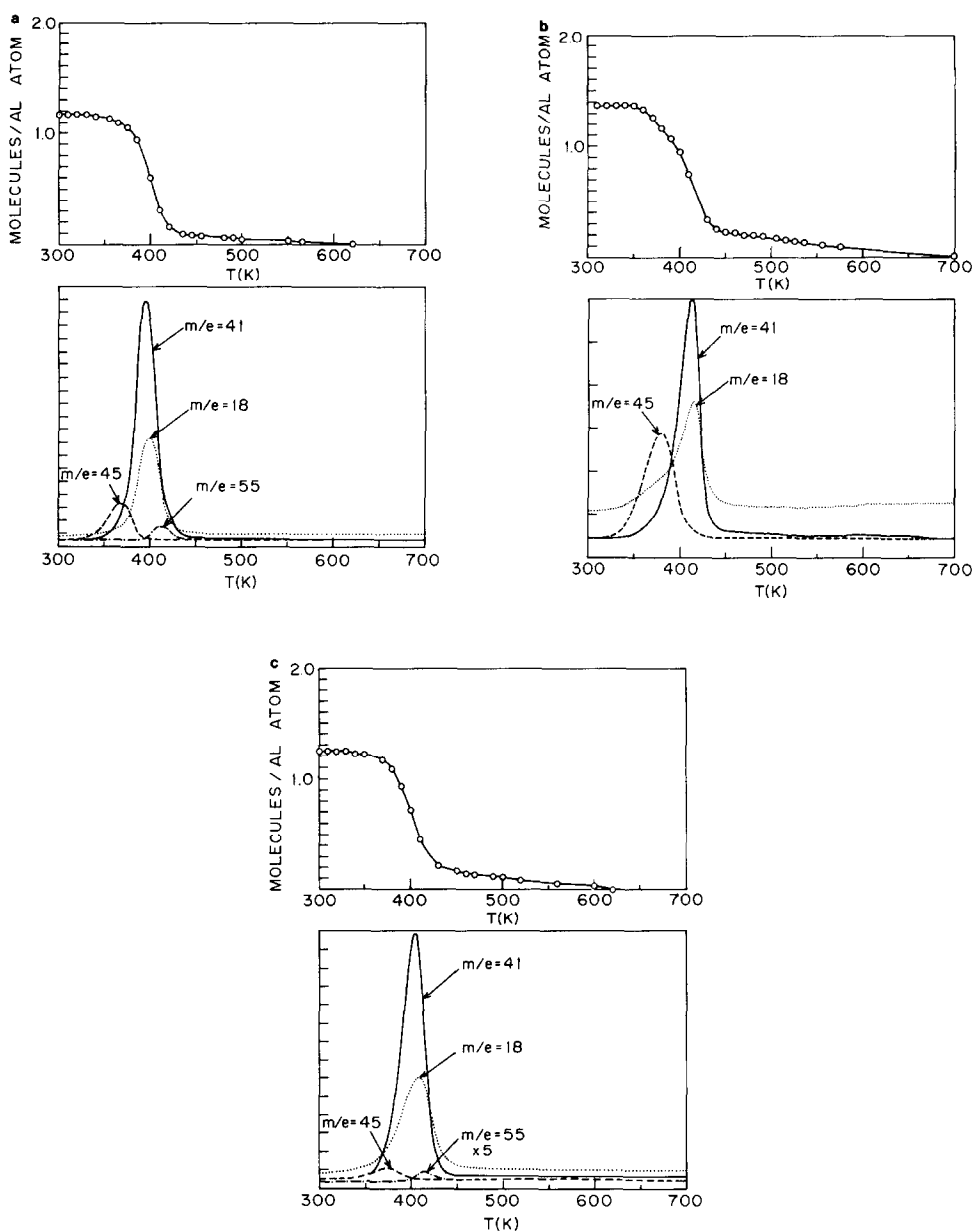[a] Assumes that each adsorbate packed at its liquid density into the zeolite.

FIG. 1. TPD and TGA results for 2-propanol on (a) H-ZSM-5, (b) H-ZSM-12, and (c) H-mordenite. On all three samples, a complex corresponding to a coverage of approximately one 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 one/Al desorbed unreacted at lower temperatures. Some oligomerization of the desorbing propene also occurred on H-ZSM-5 and H-mordenite, as shown by the presence of a peak at $m/e$ = 55 in the mass spectrum of the desorbing products.

The alcohol corresponding to the 1 : 1 adsorption state on each of the zeolite samples desorbed as propene ($m/e$ = 41) and water ($m/e$ = 18), with a peak temperature between 400 and 415 K. While peak temperatures in TPD can be influenced by a number of factors (16), the fact that the 1 : 1 complex formed by 2-propanol and the Al

site decomposes and desorbs as propene and water at approximately the same temperature on each of the zeolites is strong evidence that the complex is identical in each case. We had previously shown that the 1 : 1 adsorption complexes in H-ZSM-5 were unaffected by changing the $SiO_2/Al_2O_3$ ratio between 38 and 520 (8). Our present results imply that the structure of the crystal lattice in which the Al atoms are located also has no major effect on the stability and reactivity of the complexes formed with 2-propanol.

In addition to propene and water, a small desorption feature due to the formation of higher molecular weight, olefin products ($m/e = 55$) was observed at 425 K on the H-ZSM-5 and mordenite samples. Since butenes and larger olefins have major peaks at both $m/e = 41$ and $m/e = 55$ in their mass spectra, the presence of the peak at 55 amu indicates that some of the olefins desorbing above 420 K on the ZSM-5 and mordenite samples had undergone secondary reac-

tions. In our previous study in which we examined the effect of $SiO_2/Al_2O_3$ ratio on the adsorption of 2-propanol in H-ZSM-5, we showed that the extent to which secondary oligomerization occurs during desorption from the 1 : 1 complexes is strongly dependent on the concentration of Al sites (8). Since the $SiO_2/Al_2O_3$ ratios for the ZSM-5 and mordenite samples were slightly lower than that for the ZSM-12 sample, secondary reactions were probably less important on the ZSM-12. The fact that both the extent of oligomerization and the temperature at which products were observed were similar for the H-mordenite and H-ZSM-5 samples, both of which had a $SiO_2/Al_2O_3$ ratio close to 70, suggests that the rate and product distribution in the oligomerization chemistry of propene under the conditions of our experiment are also relatively insensitive to crystal structure.

The results for 2-propanamine on H-ZSM-5 and H-ZSM-12 are shown in Fig. 2. After saturation exposures, we were unable
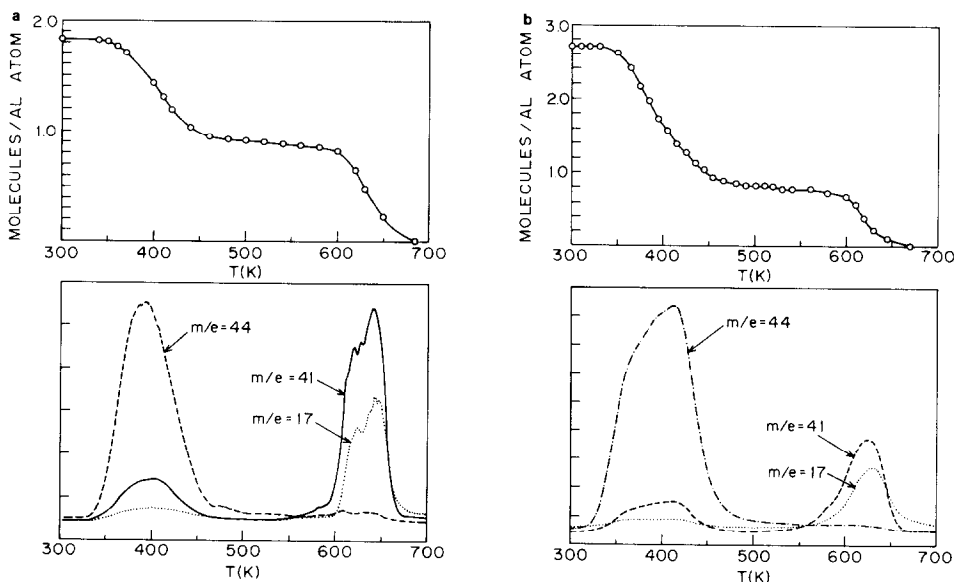


FIG. 2. TPD and TGA results for 2-propanamine on (a) H-ZSM-5 and (b) H-ZSM-12. On both zeolite samples, a desorption state corresponding to a coverage of approximately one/Al can be identified which desorbs as propene ($m/e = 41$) and ammonia ($m/e = 17$) between 600 and 650 K. 2-Propanamine adsorbed at a coverage above one/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.

to evacuate to a coverage of one/Al in reasonable times on H-ZSM-5, with between one and two molecules/Al sites still remaining in this zeolite after 20 h evacuation. The results in Fig. 2b for H-ZSM-12 were obtained after only 3 h evacuation. Not surprisingly, somewhat more 2-propanamine remained at the start of this experiment. However, additional 2-propanamine molecules above one/Al for H-ZSM-5 and above 0.8/Al for H-ZSM-12 desorbed unreacted ($m/e = 44$) in a broad feature below 500 K on both zeolites. The remaining adsorbate molecules are part of a clearly defined adsorption state which is stable over a wide temperature range. Since the coverage of 2-propanamine in the high-temperature state is one/Al within the accuracy of our TGA and Al concentration measurements, we believe the molecules associated with this state form a 1 : 1 complex with the Al sites. Also on both zeolites, the 1 : 1 complex which remains on the surface desorbs between 600 and 650 K as propene ($m/e = 41$) and ammonia ($m/e = 17$). This chemistry is well known for quaternary ammonium hydroxides in solution where it is the last step of the Hofman degradation sequence (24). Since the desorption peak temperatures at which propene (peak temperature of 400 K in TPD of 2-propanol) and ammonia (peak temperature of ~500 K under the conditions of our experiment) are observed in other experiments is well below the temperature at which they are observed following 2-propanamine adsorption (8), the desorption curves in Fig. 2 must be a measure of the decomposition reaction. The fact that this reaction takes place at the same temperature on both zeolites again points toward sites of similar activity on these two zeolites.

## DISCUSSION

In previous work, we showed that complexes consisting of one molecule/Al atom could be formed by the adsorption of simple alcohols or 2-propanamine in H-ZSM-5. The decomposition temperature and prod-

uct distribution obtained on heating these complexes were consistent with simple, acid-catalyzed chemistry and were unaffected by Al concentration (8). The implication of that work is that adsorption leading to chemical reaction in the H-ZSM-5 lattice occurs at isolated and chemically equivalent acid sites. Our present results represent a further generalization of those conclusions about the acid sites in zeolites. They suggest that the adsorption and chemistry that occurs at Brønsted acid sites associated with the lattice Al atoms are also insensitive to the crystal structure of the zeolite lattice. Adsorption complexes in the three zeolites we have examined display the same 1 : 1 adsorption stoichiometries and the same reactivities for the dehydration of 2-propanol, the degradation of 2-propanamine, and, apparently, the oligomerization of propene. All of this implies that the acid sites associated with isolated, tetrahedral Al atoms in a zeolite lattice have a characteristic proton-transfer chemistry that is determined largely by local structural influences and is independent of the extended lattice structure.

The identical, structure-independent nature of the tetrahedral Al acid sites has been suggested previously by reaction rate measurements. For $n$-hexane cracking on both H-ZSM-5 (9) and dealuminated H–Y zeolites with $SiO_2/Al_2O_3$ ratios greater than 9 (17), the activity has been shown to increase linearly with Al content for carefully prepared samples. Furthermore, the specific rates per Al site which were reported for this reaction on H-ZSM-5 and H–Y were virtually identical when the reaction was carried out under the same pressure and temperature conditions (18). These conclusions do not extend to zeolites with lower silica–alumina ratios or to materials which have not been properly pretreated to leave isolated, tetrahedral Al atoms. For example, in the above-mentioned study of $n$-hexane cracking on dealuminated Y zeolites, it was shown that the linear relationship between activity and Al content was

not valid for zeolites with more than 35 Al/ unit cell ($SiO_2/Al_2O_3 < 9$), implying that other factors must be important at higher Al concentrations (*19*). Harsh pretreatment conditions may also influence the acid sites. For example, significant increases have been observed for *n*-hexane cracking activities in H-ZSM-5 samples which have been steamed at high temperatures (*9*). While the sites responsible for the increased activities in these steamed samples are unknown, it is probable that they involve either a combination of framework and nonframework Al atoms (*9*) or that a new type of Al site, such as has been suggested by 27 Al NMR studies (*20, 21*), is formed by steaming. Similar sites may be responsible for the superacidity which has been observed for H-mordenites (*22*). In the work which we have discussed in this paper, we have attempted to avoid pretreatment conditions which could lead to these complications.

The chemistry that we have examined represents only the first stages of the multistep reaction sequences that may occur in high-pressure, reaction environments. While these simplified conditions are useful for characterizing the interactions that occur during chemisorption, they may not be sensitive to other features that are important under catalytic reaction conditions. For example, adsorption/desorption experiments are much less sensitive to small concentrations of superactive sites than reaction rate measurements would be. Second, bimolecular reactions, such as hydride transfer reactions in hydrocarbon cracking, are attenuated by these low-pressure conditions. These considerations may be responsible for some of the differences in the conclusions reached in this study and another recent comparison between zeolite structures (*23*).

In summary, the following generalizations can be applied to this and our previously published work:

(1) For a range of organic functional groups, the first adsorbate molecule per framework Al has special adsorption stability.

(2) In contrast to the clear difference in binding energy between 1 : 1 complexes and adsorption states attained at greater filling, the binding energy range among 1 : 1 complexes in three different zeolites is small.

(3) The driving force for strong binding and induced chemistry of the adsorbate is proton transfer.

(4) Local structure factors dominate these chemical interactions.

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