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Stoichiometric Adsorption Complexes in [B]- and [Fe]-ZSM-5 Zeolites[1]

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The adsorption of ammonia, 2-propanamine, and 2-propanol on H-[B]-ZSM-5 and H-[Fe]-ZSM-5 has been examined using temperature-programmed desorption (TPD) and thermogravimetric analysis (TGA) to investigate the effect of the incorporation of trivalent ions into the zeolite framework. For each of the adsorbates on H-[Fe]-ZSM-5, clearly defined adsorption complexes corresponding to one molecule/Fe atom could be identified. An adsorption complex with a stoichiometry of one molecule/B atom could also be observed for 2-propanamine on H-[B]-ZSM-5 but complexes were less clearly defined for ammonia and 2-propanol. The reactivity of these 1 : 1 complexes indicates that the acid sites formed by the hydroxyls associated with B incorporation are much weaker than those associated with Fe or Al. We also examined a sample of ZSM-5 which had extraframework Fe using 2-propanamine adsorption and found that there was negligible adsorption due to these sites. These results indicate that TPD–TGA measurements of selected adsorbates are valuable in characterizing the materials created by the incorporation of trivalent cations into the zeolite framework.

INTRODUCTION

In a series of recent papers, we have examined the acid sites in high-silica zeolites by measuring the adsorption and desorption of adsorbates which can undergo classical, acid-catalyzed reactions (*1–9*). The most important result of this work was the observation of well-defined adsorption complexes corresponding to one molecule per Al site for a range of organic molecules including a series of simple alcohols, toluene, 2-propanamine, and 2-propanone. These 1 : 1 adsorption complexes were found to be unaffected by aluminum concentration and zeolite structure (*6, 7*). Furthermore, the molecules in the 1 : 1 complexes exhibited unimolecular reactivities which were consistent with solution-phase, Brønsted-acid-catalyzed chemistry.

Recently, the incorporation of other trivalent cations, including boron and iron, into tetrahedral positions in the zeolite framework has attracted a great deal of attention due to the fact that the acidity associated with these sites is expected to differ from the acidity associated with Al sites (*10–14*). However, characterization of the acid sites in these new materials is complicated by the fact that some of the added trivalent cations may be outside the zeolite framework (*13, 15, 16*) and that activities measured in catalytic studies may be due to residual Al (*12*). The goal of this present work was to determine whether the adsorption techniques we have developed to study the acid sites in Al zeolites could be extended to the study of these other materials. Specifically, we wished to determine whether stoichiometric adsorption complexes could also be observed in zeolites in which iron and boron were present in the zeolite framework and whether reactivity differences could be observed between these complexes. If 1 : 1 adsorption complexes could be identified, the combined use of temperature-programmed desorption (TPD) and thermogravimetric analysis

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(TGA) would provide a convenient method of confirming the incorporation of trivalent cations into framework positions and for examining their relative reactivities.

We report in this paper that 1 : 1 adsorption complexes can be identified following adsorption of ammonia, 2-propanamine, and 3-propanol on H-[B]-ZSM-5 and H-[Fe]-ZSM-5, just as has been reported previously for H-[Al]-ZSM-5. In the case of H-[Fe]-ZSM-5 and H-[Al]-ZSM-5, these complexes are clearly defined in the TPD–TGA results, with the molecules associated with the 1 : 1 state either desorbing at a higher temperature than physically adsorbed species or undergoing an acid-catalyzed, unimolecular decomposition. The 1 : 1 complexes with H-[B]-ZSM-5 are more difficult to identify since the adsorbates are much more weakly bound and always desorb unreacted; however, comparison to ZSM-5 samples with no B allowed the identification of adsorption states associated with B sites as well. These results suggest that TPD–TGA measurements of simple alcohols and amines provide a useful tool for characterizing sites created by the substitution of various heteroatoms for silicon in zeolite structures.

EXPERIMENTAL

Sample Preparation and Characterization

The sample of [B]-ZSM-5 was prepared in a hydrothermal system by adding solutions of TPA-Br and sodium hydroxide to a mixture of Ludox HS-30, water, and boric acid. [Fe]-ZSM-5 samples were synthesized by a modification of a procedure described previously (*13*). Ludox HS-30 and TPA-Br were added sequentially to an acidic solution of $Fe(NO_3)_3 \cdot 9H_2O$. A NaOH solution was then added slowly to the mixture until the pH was approximately 9.5. Crystallization of both zeolites was carried out in unstirred, Teflon-lined autoclaves at 175°C for 4–5 days. The samples were then rinsed, dried, washed with a 2 *M* NaOH solution to remove any amorphous material, 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 indicated that the resulting [B]-ZSM-5 particles were spherical agglomerates, approximately 30 μm in diameter, made up of smaller crystals. The [Fe]-ZSM-5 samples were light tan in color and consisted of twinned rectangular crystals approximately 10 μm in length and 1 μm in width which formed agglomerates approximately 20 μm in diameter.

TABLE 1

Properties of Zeolite Samples Used in This Study

Sample	SiO_2/T_2O_3	Hexane adsorption		Unit cell volume ($Å^3$)
		g/100 g	cm^3/100 g[a]	
[B]-ZSM-5	85	11.4	0.17	5251
[Fe]-ZSM-5	140(1000)[b]	10.2	0.15	5382
[Al]-ZSM-5	70[c]	11.7	0.17	5382
ZSM-5(880)	—[d]	13.1	0.19	5364

[a] Assumes that adsorbate packed at its liquid density into the zeolite.
[b] Residual SiO_2/Al_2O_3 measured by ICP.
[c] Measured by ^{27}Al NMR (*17*).
[d] Not directly measured in this study.

The elemental analysis, hexane adsorption, and x-ray diffraction results for the samples used in this paper are listed in Table 1. The x-ray diffraction peaks were sharp, with no amorphous background and no peaks other than those due to ZSM-5 observed. Elemental analysis of the Fe and B samples was performed by Galbraith Laboratories, Inc. (Knoxville, TN) using an inductively coupled plasma (ICP) and gave concentrations close to those predicted based on gel concentrations. Evidence that the B was incorporated into the zeolite framework is provided by x-ray diffraction data in which the unit cell dimensions corresponded to a SiO_2/B_2O_3 ratio of 50 based on the equation developed by Meyer *et al.* (*16*). The unit cell dimensions determined for the [Fe]- and [Al]-ZSM-5 samples were also consistent with published values (*15*). TPD–TGA results provide additional strong evidence for the incorporation of the B and Fe into the framework, as will be discussed later. The samples were also characterized by hexane adsorption measurements to estimate the pore volume and compare it to the expected porosity of ZSM-5, 0.19 cm^3/g.

Two samples of Al-containing ZSM-5, donated by the Mobile Oil Company, with SiO_2/Al_2O_3 ratios of 70 and 880, were used for comparison in this study. These samples are designated H-[Al]-ZSM-5 and ZSM-5(880), respectively, in this paper. The Al concentration in the [Al]-ZSM-5 sample was checked by ^{27}Al NMR, as discussed previously (*17*). This material was obtained as an NH_4-ZSM-5 powder and heated *in vacuo* to 700 K to convert it to the hydrogen form. Electron microscopy indicated that the material consisted of particles uniformly between 0.4 and 0.5 μm and the x-ray diffraction data were consistent with the published data for ZSM-5 (*18*).

TPD and TGA measurements on the ZSM-5(880) sample were performed to separate physically adsorbed states from molecules which were associated with 1 : 1 adsorption complexes in the other zeolites. This sample was characterized by only x-ray diffraction, *n*-hexane adsorption, and electron microscopy. The x-ray diffraction measurements were consistent with published data for ZSM-5 and the material was found to consist of particles approximately 1 μm in size. While we did not directly measure the SiO_2/Al_2O_3 ratio, adsorption uptakes indicated that the Al concentration was at least as low as that reported by Mobil. Also, no ion exchanges were performed on this sample and there may have been incomplete protonation of the Al sites.

Adsorption Measurements

The equipment and procedures used to measure adsorption were the same as those used in previous papers (*1–8*). TPD and TGA experiments were carried out simultaneously in a high-vacuum chamber equipped with a Cahn 2000 microbalance and a Spectramass quadrupole mass spectrometer. This system could be evacuated with a turbomolecular pump to a base pressure below 1×10^{-7} Torr. Approximately 17 mg of zeolite was spread over the flat sample pan of the microbalance to avoid bed effects in adsorption and desorption (*19*). The heating rate for the TPD–TGA experiments was maintained at 10 K/min by a feedback controller, and a thermocouple placed near the sample was used for temperature measurement. During the desorption experiment, the sample weight was continuously monitored using the microbalance and the desorbing gases were observed using the mass spectrometer which was interfaced with a microcomputer to allow several mass peaks to be measured simultaneously. In initial TPD experiments, the mass range 10–70 m/e was examined at 15 K intervals to identify the products which were formed. The desorption experiments were then repeated using the computer to monitor the major mass peaks which could be used to identify each product. The mass peaks monitored were the most intense peaks in the fragmentation patterns of ammonia (m/e = 17), 2-propanamine (m/e = 44), 2-propanol (m/e = 45), water (m/e = 18), and propene (m/e = 41).

For most of the adsorption experiments, the samples were exposed to between 3 and 15 Torr of the adsorbate of interest at 295 K for approximately 5 min. 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 following this treatment, as shown in Table 2 for 2-propanamine and 2-propanol on each of the different samples. TPD–TGA measurements were performed following evacuation of the samples to remove weakly adsorbed molecules. However, for 2-propanol and ammonia adsorption on H-[B]-ZSM-5, it was necessary to place an ice bath around the sample during the evacuation procedure since essentially all of the adsorbate molecules could be

TABLE 2

Saturation Gravimetric Uptakes Measured at 295 K Using Exposures Discussed in the Text

Sample	2-Propanol		2-Propanamine	
	g/100 g	cm^3/g^a	g/100 g	cm^3/g^a
[B]-ZSM-5	12.6	0.16	10.8	0.16
[Fe]-ZSM-5	10.9	0.14	9.1	0.13
[Al]-ZSM-5	13.9	0.18	10.7	0.15
ZSM-5(880)	12.8	0.18	11.5	0.17

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

evacuated at 295 K. On each of the samples for each of the adsorbates, over the course of an experimental sequence involving one adsorption/desorption cycle, the total mass change was found to be negligible, indicating that no residual products were left undetected in the zeolite.

RESULTS

TPD–TGA results for ammonia, 2-propanamine, and 2-propanol are shown in Figs. 1–3. Because the adsorbate molecules associated with a 1 : 1 coverage on the H-[B]-ZSM-5 desorbed unreacted in a temperature range similar to that observed for physically adsorbed species, the results obtained for the ZSM-5(880) sample, using similar adsorption and evacuation conditions, are shown together with the H-[B]-ZSM-5 results for comparison. We discuss the results for each adsorbate individually.

Ammonia

The TPD–TGA results for NH_3 on H-[B]-ZSM-5 and ZSM-5(880) following saturation exposures at 295 K and extended evacuation at 273 K (2–4 h) are shown in Fig. 1a. It was necessary to cool the H-[B]-ZSM-5 samples to 273 K during evacuation since the sample weight could not be stabilized at 295 K until essentially all of the NH_3 had desorbed. While the presence of an adsorption state with a coverage of one molecule/B atom is not directly apparent from the results on H-[B]-ZSM-5, comparison of these results with those on ZSM-5(880) shows that the H-[B]-ZSM-5 sample does have an increased affinity for NH_3. Following adsorption and evacuation of 4 h at 273 K, the NH_3 coverage on H-[B]-ZSM-5 was 0.7 g/100 g compared to 0.3 g/100 g on ZSM-5(880) after 2 h of evacuation under the same conditions. During TPD–TGA measurements, the ammonia on the H-[B]-ZSM-5 sample desorbed in a well-defined peak centered at approximately 370 K, while the TGA results on ZSM-5(880) showed only a gradual weight decline over the temperature range of our experiments. This relatively weak association of NH_3 with the B sites has been observed previously (*10*). While the desorption temperatures we observed are lower than those reported previously for H-[B]-ZSM-5, this is almost certainly due to the experimental conditions used in these measurements (*19*).

On H-[Fe]-ZSM-5 and H-[Al]-ZSM-5, evacuation below a coverage of one molecule/Fe or Al atom was not possible in reasonable times, even at 295 K. While the amount of NH_3 remaining in the sample was found to be a function of evacuation time, NH_3 present in excess of the 1 : 1 coverage desorbed at lower temperatures in TPD on both samples and varying the evacuation time only changed the amount of NH_3 observed in these low-temperature features. The TPD–TGA results reported in Figs. 1b and c were obtained following 15 h evacuation and show only small desorption features at lower temperatures. NH_3 associated with a 1 : 1 coverage desorbed in separate, well-defined peaks centered at approximately 480 K on H-[Fe]-ZSM-5 and 500 K on H-[Al]-ZSM-5. As with H-[B]-ZSM-5, these desorption temperatures for NH_3 are somewhat lower than have been reported previously on H-ZSM-5 with tetrahedral Fe or Al in the structure (*10*). This is almost certainly due to differences in the experimental conditions used, since peak temperatures reported in the literature for

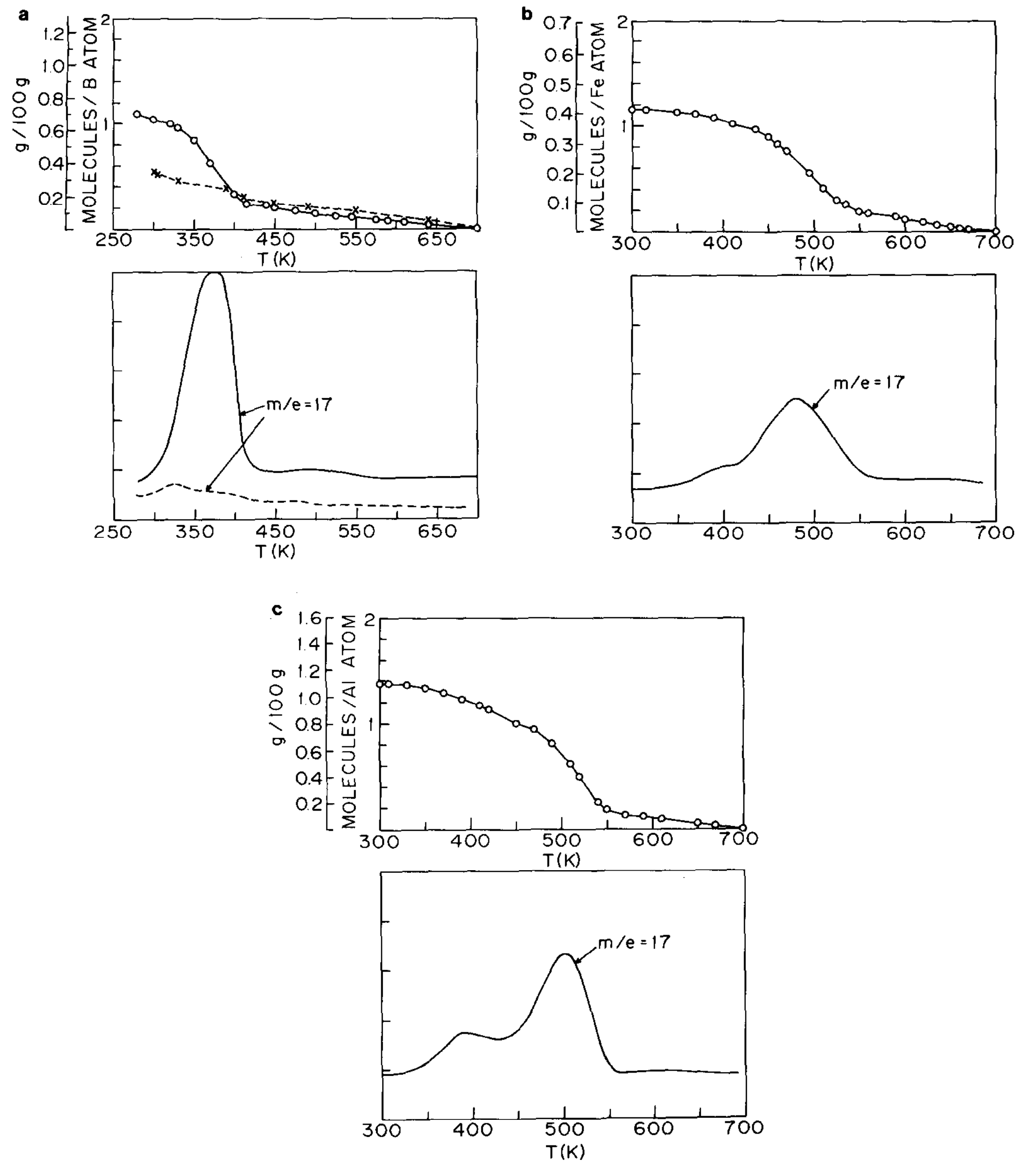

FIG. 1. TPD–TGA results for ammonia on (a) H-[B]-ZSM-5 following evacuation at 273 K for 4 h and ZSM-5(880) (dashed line) following evacuation at 273 K for 2 h; (b) H-[Fe]-ZSM-5 following evacuation at 295 K for 15 h; (c) H-[Al]-ZSM-5 following evacuation at 295 K for 15 h. On H-[B]-ZSM-5, NH_3 (*m*/*e* = 17) desorbs in a well-defined peak centered at 370 K, while on ZSM-5(880), TGA shows only a gradual weight decline. NH_3 associated with a 1 : 1 coverage desorbs in a peak centered at 480 K on H-[Fe]-ZSM-5 and at 500 K on H-[Al]-ZSM-5.

H-[Al]-ZSM-5 samples vary between 600 and 700 K (*10, 21–24*). Our results are consistent with previous work in that the peak temperatures observed for the Fe sample are somewhat lower than those for the Al sample. However, since NH_3 peak temperatures in TPD can be affected by a number of factors, including adsorption site densities and particle sizes (*19*), the difference in peak temperatures for the H-[Fe]-ZSM-5 and H-[Al]-ZSM-5 may or may not represent a meaningful difference in the strength of the acid sites on these two materials.

2-Propanamine

The formation of clearly defined, 1 : 1 adsorption complexes is more easily observed for 2-propanamine, as shown by the TPD–TGA curves in Fig. 2. In these experiments, the samples were saturated with 2-propanamine and then evacuated. While evacuation time did affect the initial coverages, we found that 2-propanamine was very difficult to remove from the samples by evacuation at room temperature and substantial coverages were always present at the beginning of a run, even for the ZSM-5(880) sample. However, this physically adsorbed 2-propanamine desorbed unreacted in a separate, low-temperature feature centered below 400 K. This feature is present on all of the samples, including the ZSM-5(880) sample shown in Fig. 2a.

On each of the other zeolite samples, a second desorption feature corresponding to a coverage of close to one molecule per B, Fe, or Al atom is clearly observed, as shown by the TPD–TGA curves in Figs. 2b–d. On H-[B]-ZSM-5, desorption from a coverage of close to one molecule/B occurs in a second peak of unreacted 2-propanamine centered at approximately 550 K. On H-[Fe]-ZSM-5 and H-[Al]-ZSM-5, 2-propanamine adsorbed at a coverage close to one molecule/Fe or Al atom desorbed as propene and ammonia between 600 and 650 K. The stoichiometry of adsorption in the high-temperature state on the H-[Fe]-ZSM-5 sample actually appears to be between 0.8 and 0.9 molecule/Fe. Due to uncertainties in the Fe concentration measurements and the possibility that some of the Fe may not be present in the zeolite framework in our sample, we believe the adsorption stoichiometry corresponding to the desorbing propene and ammonia is one molecule/framework Fe. We interpret this well-defined desorption feature as corresponding to a 1 : 1 adsorption complex between 2-propanamine and the hydroxyls associated with Fe atoms in the zeolite lattice. Since the temperature range for the desorption of the 1 : 1 complex is well above that for either ammonia or propene desorption on either zeolite (*3*), these desorption curves must be a measure of a decomposition reaction. Since the products of this decomposition reaction are similar to those observed in a Hofmann elimination, the 1 : 1 adsorption complexes for 2-propanamine on both H-[Fe]-ZSM-5 and H-[Al]-ZSM-5 are probably protonated up to the reaction temperature. The fact that the decomposition reaction occurs at the same temperature on both types of zeolite does not indicate that the acid sites associated with Al and Fe are identical. The reaction is probably limited by the decomposition of the isopropyl ammonium ion and both H-[Fe]-ZSM-5 and H-[Al]-ZSM-5 appear to contain acid sites which are strong enough to maintain the ion up to a temperature at which the decomposition will occur. In contrast, 2-propanamine associated with a 1 : 1 coverage in H-[B]-ZSM-5 may also be protonated at lower temperatures; but, if it is, the equilibrium distribution is shifted toward the amine at temperatures low enough to prevent reaction and allow desorption of the unreacted amine.

It is appropriate to mention at this point that the observation of well-defined adsorption states corresponding to a coverage of one molecule/Fe or B atom strongly implies that most of the Fe and B are tetrahedrally coordinated and in the zeolite framework. The evidence is particularly strong for the H-[Fe]-ZSM-5 sample since the acid-catalyzed decomposition of 2-propanamine implies that Brønsted acid sites are generated by the presence of the Fe atoms in a quantity close to one molecule/Fe atom. To test this idea further, we examined a sample of ZSM-5 which contained Fe not in the lattice framework. This sample was prepared by heating the [Fe]-ZSM-5 sample in air at 873

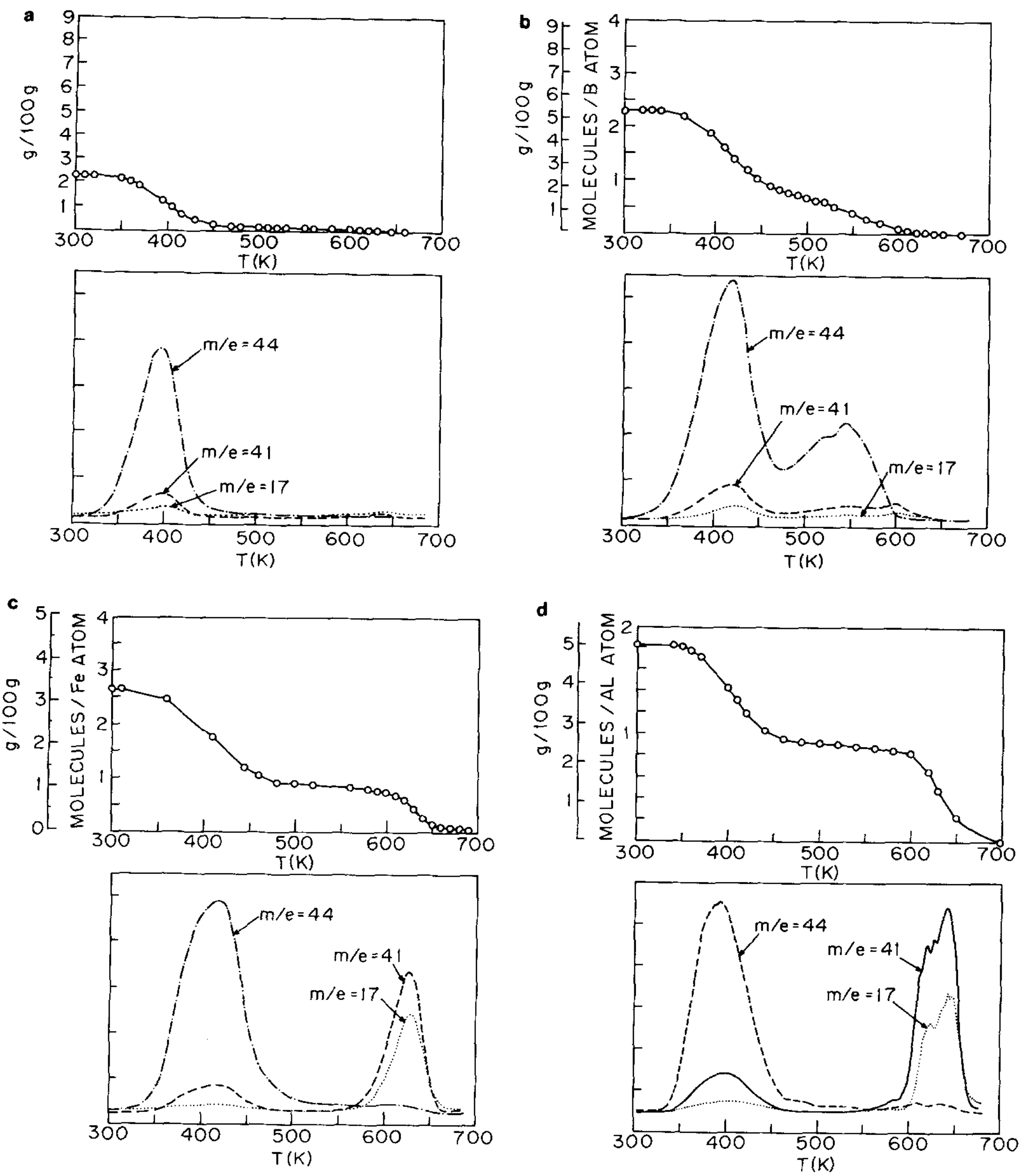

FIG. 2. TPD–TGA results for 2-propanamine on (a) ZSM-5(880) following evacuation for 4 h; (b) H-[B]-ZSM-5 following evacuation for 4 h; (c) H-[Fe]-ZSM-5 following evacuation for 15 h; (d) H-[Al]-ZSM-5 following evacuation for 15 hr. On each sample, 2-propanamine (m/e = 44) desorbed unreacted in a peak centered at approximately 400 K in an amount which depended on the evacuation time. (Peaks at m/e = 17 and 41 are also present in the fragmentation pattern of 2-propanamine.) On samples b–d, a second desorption feature which corresponds to one molecule per B, Fe, or Al atom is also observed. On H-[B]-ZSM-5, this 1 : 1 state desorbs as unreacted 2-propanamine at 550 K. On H-[Fe]-ZSM-5 and H-[Al]-ZSM-5, the 1 : 1 state desorbs as propene (m/e = 41) and ammonia (m/e = 17) between 600 and 650 K. The multiple peaks in the high-temperature feature of d are due to oscillations in the heating rate at this temperature.

K for 2 h. The sample treated in this manner turned light brown in color, and x-ray diffraction data showed a change in the unit cell volume toward that of the ZSM-5(880) sample. TPD–TGA results for 2 propanamine on this modified sample indicated an 80% decrease in the amounts of propene and ammonia that were formed between 600 and 650 K. This implies that Fe could be removed from the framework by heating in air and that 1 : 1 adsorption complexes are not formed by Fe atoms which are not part of the zeolite lattice. Since it is frequently difficult to determine whether or not substituents have been incorporated into the framework, our results suggest that TPD–TGA measurements of molecules like 2-propanamine may provide a useful tool for this purpose.

2-Propanol

In our previous studies on high-silica zeolites containing Al, we found that 2-propanol adsorption provided some of the clearest evidence for a 1 : 1 adsorption complex (*3*). In experiments on H-ZSM-5 samples with SiO_2/Al_2O_3 ratios between 38 and 520 (*6*) and on high-silica samples of H-ZSM-12 and H-mordenite (*7*), we found that 2-propanol adsorbed in excess of one molecule/Al atom desorbed unreacted below 400 K, while 2-propanol adsorbed at a coverage of one/Al desorbed as propene and water at 400 and 405 K, respectively. Our present results with 2-propanol on the Fe- and B-containing samples suggest that there is also a tendency to form adsorption complexes on these materials.

Figures 3a and b show the TPD–TGA results for ZSM-5(880) and H-[B]-ZSM-5, respectively. As with NH_3, 2-propanol adsorbed very weakly on these two samples. It was again necessary to cool the sample to 273 K during evacuation since we were unable to stabilize the coverage of 2-propanol at 295 K until most of the alcohol had desorbed. However, for evacuation at 273 K, the coverage leveled off at 1.2 g/100 g on the ZSM-5(880) sample and at 3.0 g/100 g (1.3 molecules/B atom) on the H-[B]-ZSM-5 sample after 4 h evacuation. On both samples, the 2-propanol desorbed unreacted from a broad feature centered at approximately 360 K. Clearly, the similarity in the results for both the ZSM-5(880) and the H-[B]-ZSM-5 samples and the lack of any reaction chemistry during desorption imply that the affinity of 2-propanol for the hydroxyl sites associated with B must be very weak. However, we believe that the differences in the final coverages following evacuation do imply some affinity between the 2-propanol and the B-sites. More work will be needed to confirm this.

Affinity between 2-propanol and sites formed by incorporating Fe into the ZSM-5 lattice is much easier to observe, as shown in Fig. 3c. Following saturation of the sample with 2-propanol and evacuation for 15 h at 295 K, the coverage on the H-[Fe]-ZSM-5 sample corresponded to approximately 1.2 molecules/Fe atom. Some of this 2-propanol desorbed unreacted during TPD from a peak centered at 390 K; however, between 0.8 and 0.9 molecule/Fe desorbed as propene and water at 430 and 435 K, respectively. Shorter evacuation times resulted in more unreacted 2-propanol desorption at low temperatures, but the amounts of propene and water observed in TPD were independent of evacuation time. As discussed previously for 2-propanamine adsorption, the amounts of propene and water desorbing from the H-[Fe]-ZSM-5 sample correspond closely to a 1 : 1 adsorption complex of 2-propanol at the hydroxyl sites formed by tetrahedral Fe atoms in the zeolite lattice.

A comparison of results for 2-propanol on H-[Fe]-ZSM-5 and H-[Al]-ZSM-5 suggests that the acid sites in these two zeolites are very similar. In both cases, 1 : 1 complexes are formed and these 1 : 1 complexes desorb as propene and water. However, the temperatures at which propene and water are formed with H-[Fe]-ZSM-5 appear to be slightly higher than were observed with H-[Al]-ZSM-5 (*3*). While desorption tempera-

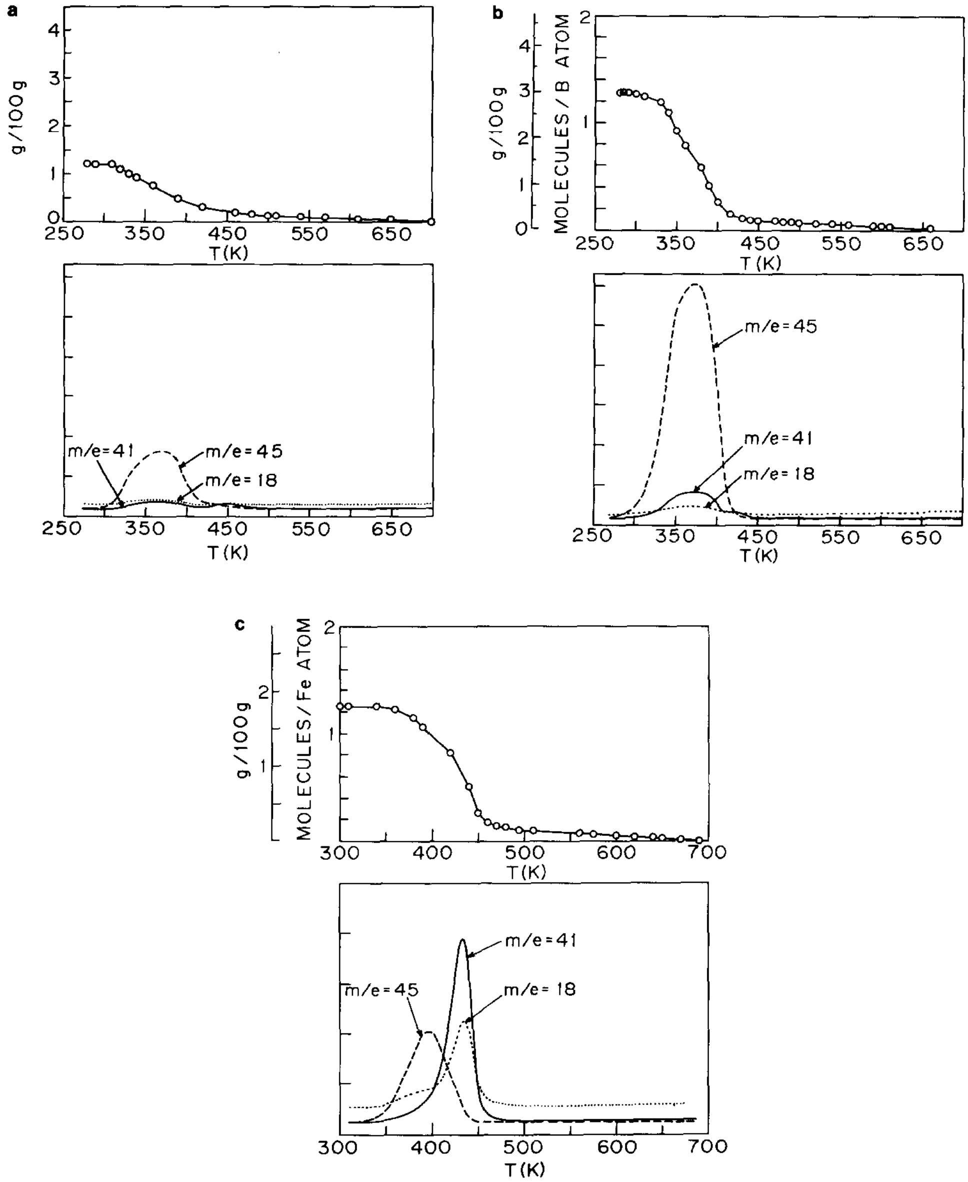

FIG. 3. TPD–TGA results for 2-propanol on (a) ZSM-5(880) following 4 h evacuation at 273 K; (b) H-[B]-ZSM-5 following 4 h evacuation at 273 K; (c) H-[Fe]-ZSM-5 following 15 h evacuation at 295 K. On both ZSM-5(880) and the H-[B]-ZSM-5 samples, 2-propanol desorbed unreacted in a broad feature (*m/e* = 45) centered at 360 K; however, the difference in coverage following evacuation implies some affinity of 2-propanol for the B sites. On the H-[Fe]-ZSM-5 sample, a desorption state corresponding to close to one molecule per Fe atom can be identified which desorbs as propene (*m/e* = 41) and water (*m/e* = 18). 2-Propanol (*m/e* = 45) adsorbed in excess of one molecule per Fe atom desorbed unreacted at lower temperatures.

tures in porous materials can be affected by transport properties and readsorption effects and should be interpreted with caution, the appearance of propene and water in the TPD curves is probably limited primarily by the temperature at which 2-propanol decomposes and may not be as strongly affected by the experimental conditions. Therefore, the increased desorption temperatures on H-[Fe]-ZSM-5 may indicate that this zeolite has slightly weaker acid sites than H-[Al]-ZSM-5.

DISCUSSION

The results discussed in this paper show that the 1 : 1 adsorption stoichiometry observed between a wide range of adsorbates and the Al sites in high-silica zeolites can also be observed for zeolites in which Fe has been substituted into the tetrahedral framework. This 1 : 1 adsorption stoichiometry can also be observed with B sites for strongly basic molecules like amines, but the strength of the acid sites in H-[B]-ZSM-5 appears to be too weak to form well-defined complexes with weaker bases like alcohols or even ammonia.

The acid sites in each of the materials in this study are almost certainly associated with hydroxyl groups present at the tetrahedral B, Fe, or Al positions in the zeolite framework. In recent adsorption studies on Al-containing H-ZSM-5 (*3, 5*), the reactivity of a series of molecules and the relative ability of pairs of molecules to compete for sites in the zeolite were shown to correlate well with the gas-phase, proton affinities. This implies that proton transfer from the zeolite to the adsorbate molecule plays an important role in forming these 1 : 1 adsorption complexes. Differences in the ability of B-, Fe-, and Al-containing zeolites to form 1 : 1 adsorption complexes for a given molecule like 2-propanol, therefore, are related to differences in these hydroxyl groups. Other evidence for this comes from the work of Chu and Chang (*10*), who reported a correlation between the desorption peak temperatures for ammonia and the vibrational frequency of the hydroxyl peak for isomorphous substituted H-ZSM-5 zeolites.

The extent of proton transfer to the adsorbate and the nature of the bonding between the protonated adsorbate and the zeolite framework are probably dependent on both the adsorbate and the acid site. For example, the 1 : 1 complexes formed by 2-propanamine on H-[Fe]-ZSM-5 and H-[Al]-ZSM-5 probably result in the formation of an isopropyl ammonium ion. In the case of the intermediate formed by dehydration of 2-methyl-2-propanol in H-[Al]-ZSM-5, ^{13}C-NMR measurements indicate that the intermediate is not a true carbenium ion but rather a silyl alkyl ether in which the alkyl group is covalently bonded to the zeolite lattice (*17*). In this case, proton transfer is complete but there is no formal charge on the alkyl group. For 2-propanol in H-[Fe]-ZSM-5 and H-[Al]-ZSM-5, the adsorption complex may well involve hydrogen bonding, with only incomplete transfer of the proton to the alcohol. If the increased temperatures we observed for the formation of propene and water during 2-propanol desorption from H-[Fe]-ZSM-5 compared to H-[Al]-ZSM-5 are actually a measure of the reaction rate and not due to transport properties, it may indicate that the extent of proton transfer to 2-propanol on H-[Al]-ZSM-5 is greater. The hydroxyls in H-[B]-ZSM-5 are apparently incapable of transferring a proton to 2-propanol under the conditions of our experiment.

TPD–TGA measurements of a series of different molecules also appears to provide an excellent way of characterizing the relative strengths of the acid sites generated by the incorporation of trivalent elements into the framework. These measurements are inherently less sensitive than reactor studies to the presence of residual Al (*12*) or to the types of superactive sites which are generated by steaming (*20*). From the work presented in this paper, for example, it is evident that the sites associated with B are much weaker than those associated with Al or Fe. With the adsorbates used in this paper, it is difficult to distinguish between the Al and the Fe sites. However, observed differences in the stretching frequency of hydroxyl groups in H-[Al]-ZSM-5 and H-[Fe]-ZSM-5 zeolites suggest that there are differences in acidity between these two zeolites which may be detectable if a wider range of adsorbates is examined.

CONCLUSIONS

We have demonstrated that adsorption complexes with a coverage of one molecule/trivalent substituent atom can be formed with ammonia, 2-propanamine, and 2-propanol in H-[Fe]-ZSM-5 and with 2-propanamine in H-[B]-ZSM-5. Proton transfer from the hydroxyls formed by the incorporation of B and Fe appears to play an important role in forming these adsorption complexes. While it is difficult to distinguish between the acid sites associated with Al and Fe atoms with the adsorbates used in this study, we have found that the acid sites associated with B incorporation must be much weaker than those formed by Fe or Al incorporation. Finally, the results of this study indicate that TPD–TGA techniques can be valuable in characterizing the effect of trivalent element incorporation into the zeolite framework.

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