Stoichiometric adsorption complexes of boron trichloride and antimony pentafluoride in H-ZSM-5

W.P. Fletcher III, C.S. Gilbert and A.I. Biaglow *

Department of Chemistry, United States Military Academy, West Point, NY 10996, USA

Received 14 January 1997; accepted 23 June 1997

This work demonstrates that inorganic metal halide compounds such as BCl_3 and SbF_5 can be used to prepare adsorption complexes with a stoichiometry of one molecule per Brønsted acid site in the zeolite H-ZSM-5. BCl_3–acid site complexes are prepared by saturating the zeolite with BCl_3 and then evacuating. The BCl_3 complex desorbs above 400 K, and $\sim 50\%$ of the BCl_3 remains adsorbed at temperatures above 750 K. SbF_5–acid site complexes are prepared by saturating the zeolite, evacuating, and heating to 700 K in vacuum. The SbF_5 complex is shown to polarize coadsorbed acetone to the same degree as magic acid. The stability of the metal halide complexes is further characterized with adsorption and reaction of propene and ethene to form oligomers. Small amounts ($< 10\%$) of the metal halide desorb during the oligomer desorption experiment.

Keywords: Lewis acid, Brønsted acid, zeolite, H-ZSM-5, boron trichloride, antimony pentafluoride, SbF_5, BCl_3, adsorption, acetone, NMR

1. Introduction

Mixtures of Brønsted acids such as HF or HCl with strong Lewis acids are known to catalyze many reactions involving electrophilic, electron-deficient species as intermediates [1]. Examples of this class of acids, such as fluorosulfuric acid mixed with antimony pentafluoride or ''magic acid'', have also been used to produce a wide range of stable carbocations [2–4]. There are also many potential industrial applications of these acids. One example is the Mitsubishi Gas Chemical Company's PTAL process, in which paratolualdehyde is synthesized from toluene and CO using HF/BF_3 as a catalyst [5]. However, there are serious disadvantages and hazards associated with using these extremely corrosive and poisonous materials in large-scale processes.

We have recently demonstrated that zeolites can be used in place of the proton donor, and that zeolites that are doped with aluminum trichloride are active in the carbonylation of benzene with carbon monoxide to form benzaldehyde, the Gattermann–Koch reaction [6]. In contrast to this, zeolites that are not doped with metal halides are not active in the carbonylation reaction, at least under similar experimental conditions [6]. This result suggests that the acidity of the zeolite/metal halide composite material is significantly greater than that of the pure zeolite. A significant practical advantage in this approach is that the metal halide appears to be tightly bound in the zeolite, which greatly simplifies the handling of the metal halide. Because of the large variety of metal halide Lewis acids and zeolite host materials, these composite materials offer a wealth of potential applications in heterogeneous catalysis and are very exciting to study.

Our earlier work with $AlCl_3$-promoted zeolites as well as other previous reports [6–9] raise several important questions regarding the nature of the composite material. In particular, one would like to know the specific structure of the adsorbed $AlCl_3$ molecule. It is possible that the $AlCl_3$ is coordinated at the Brønsted site in a tetrahedral complex in much the same way as HF is coordinated to BF_3 [9,10]. Alternatively, it is also possible that the adsorbed molecules are in a physisorbed state, and are free to move around inside the zeolite pores. Thermal stability is another consideration. It may be possible that the adsorbed Lewis acid is stable in the zeolite at substantial temperatures. Under these conditions, it may be possible to design catalytic processes which utilize thermal desorption of products. The properties of the adsorbed Lewis acid will largely determine the types of reactions that will be possible in these composite materials.

In this study, we have used gravimetric analysis to demonstrate that BCl_3 and SbF_5 are strongly adsorbed by the hydrogen form of H-ZSM-5. We have characterized the thermal stability of the adsorbed metal halides using thermogravimetric analysis (TGA). In all cases, we observe a desorption state with a mass that corresponds to a stoichiometry of one molecule per Brønsted acid site in the sample. In the case of SbF_5, the 1 : 1 adsorption complex is observed at temperatures above 700 K. The acidity and stability of the adsorption complexes are investigated using ^{13}C NMR of adsorbed acetone and olefin oligomerization and decomposition reactions. The picture that is developed is that of a metal halide–zeolite composite solid material with properties

* To whom correspondence should be addressed.

that are similar to those of materials such as HF/BF_3, $HCl/AlCl_3$ or HF/SbF_5.

2. Experimental

Three different H-ZSM-5 samples were examined in this study. The structure and purity of each sample was verified with powder X-ray diffraction. Each sample was calcined at 873 K in O_2, ion-exchanged in 2.0 M ammonium sulfate solution at 360 K, and heated to 770 K to obtain the hydrogen form. The sample designated H-ZSM-5A was received in the Na-form from Chemie Uetikon AG (Zeocat-Pentasil-PZ-2/54Na). Following the above pretreatment, this sample had a porosity of 0.174 cm^3/g, determined from the uptake of *n*-hexane at 14.5 Torr and room temperature, compared to the ideal pore volume of 0.19 cm^3/g. The Brønsted site concentration of this material was determined from the amount of isopropylamine which decomposes between 575 and 650 K in TGA [11–13], and was 510 μmol/g, compared to the bulk Al content, determined with atomic absorption spectroscopy, of 630 μmol/g. The sample designated H-ZSM-5B was synthesized in our lab according to published procedures [14], using tetra-*n*-propylammonium bromide as a templating agent, and having a framework Al content (estimated from the composition of the synthesis gel) of 420 μmol/g. The concentration of Brønsted sites in this material was 360 μmol/g. The sample designated H-ZSM-5C is a commercial material (Linde S115) with a Brønsted site concentration of 170 μmol/g. The TGA site characterization data are presented in figure 1.

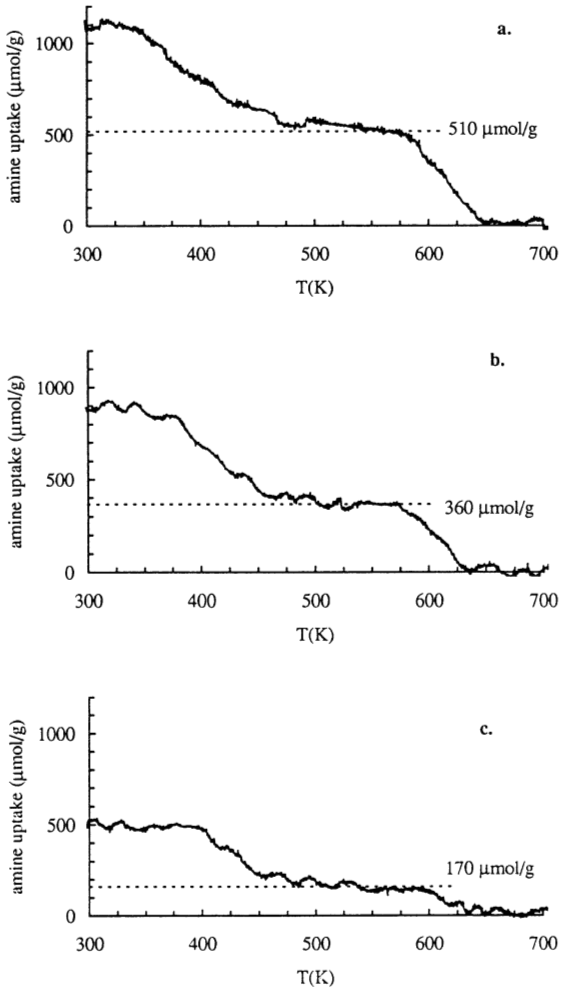


Figure 1. Results of isopropylamine TGA characterization of (a) H-ZSM-5A, (b) H-ZSM-5B, and (c) H-ZSM-5C.

Gravimetric and TGA experiments were conducted in a Perkin-Elmer TGS-2 microbalance which was evacuated to a background pressure of 1.0×10^{-5} Torr with a diffusion pump. The microbalance was equipped with a high-vacuum manifold which was used to transfer the BCl_3 vapor. Each sample was outgassed in the microbalance at 450°C until the pressure returned to its background value prior to exposure to the adsorbate. The samples were cooled to room temperature and exposed to controlled pressures of isopropylamine for site concentration measurements or to BCl_3 or SbF_5 for $\sim$ 5 min, at which time the microbalance was again evacuated prior to the TGA. The TGA of each adsorbate was conducted under vacuum with a heating rate of 20 K/min unless otherwise noted.

In an attempt to characterize the acidic properties of the metal halide-treated zeolites, we examined the ^{13}C NMR carbonyl chemical shift of acetone adsorbed in selected metal halide-treated samples. The chemical shift of the carbonyl carbon has been shown to be sensitive to the acid environment of the molecule [15–23]. Samples for NMR were weighed, placed in shallow beds in 1/2 inch horizontal glass tubes [24] on the vacuum manifold, and outgassed at 700 K until the pressure returned to the background value, $\sim$ 6 h. After cooling to room temperature, some samples were dosed with controlled volumes of ^{13}C-carbonyl-labeled acetone (Cambridge Isotopes Labs). Other samples were cooled to room temperature, and were dosed with controlled volumes of SbF_5 and then acetone. The samples were sealed in glass tubes and kept in liquid nitrogen until being warmed to room temperature and transferred to NMR rotors under an inert atmosphere.

All NMR spectra were acquired on a Brüker MSL 200 spectrometer with a ^{13}C resonance frequency of 50.323 MHz. Spectra consisted of 16 384 co-added scans with a repetition time of 3.0 s. All spectra were obtained with ^1H–^{13}C cross polarization, with a proton 90° pulse of 5 μs, a contact time of 3 ms, and a decoupled acquisition time of 40 ms. The magic angle spinning frequency was 4070 $\pm$ 15 Hz. The magnet was shimmed using adamantane until a spinning linewidth of less than 2.5 Hz was obtained. Adamantane was used as an external frequency standard, and showed daily frequency variations of less than 0.1 Hz. All spectra were processed with 20 Hz

of Lorentzian line broadening prior to the Fourier transform and are each referenced to TMS.

In order to further characterize the acidity and stability of the composite materials, we examined the adsorption and reaction of propene and ethene. Previous experiments have shown that the propene and ethene oligomerization reaction occurs readily in aluminosilicate zeolites [25,29]. Propene reacts rapidly in H-ZSM-5 at room temperature, and ethene reacts at slightly elevated temperatures. In this study, we compared the results obtained for pure, undoped H-ZSM-5 with those obtained on SbF_5-doped samples. The procedure used to introduce the olefins was identical to that used to introduce the metal halide vapors, as described above. The progress of the reaction was monitored with the weight uptake on exposure of the sample to 45 Torr of ethene or 10 Torr of propene. When the olefin oligomerization does occur, we observe a relatively large mass uptake which is irreversible on evacuation at room temperature, with desorption of the reaction products occurring between 400 and 550 K. The presence of unreacted, physisorbed olefin was indicated by the relatively easy removal of these molecules by evacuation at room temperature [25,29], which occurred in less than 1 min in our experiment.

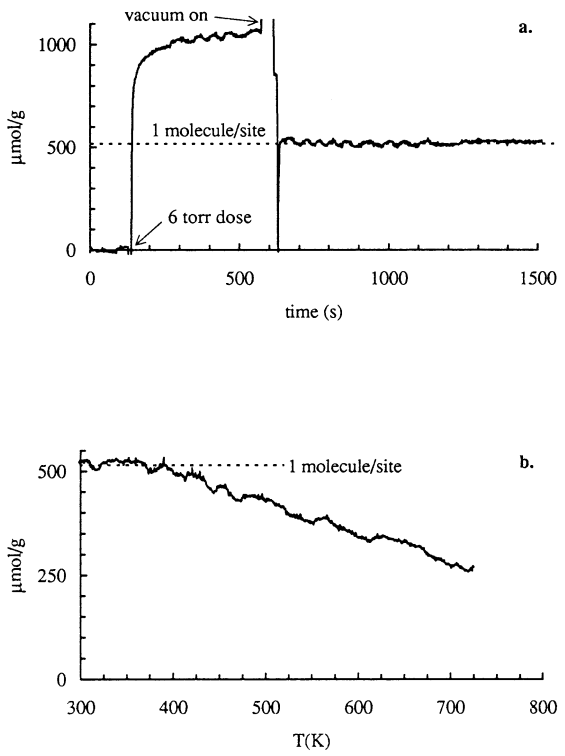


Figure 2. (a) Adsorption of BCl_3 in H-ZSM-5A. (b) TGA results for H-ZSM-5A doped with BCl_3.

3. Results

The data consists of isothermal, room temperature gravimetric adsorption data, as well as the TGA data for each of the three samples. The room temperature adsorption data show the formation of a 1 : 1 adsorption complex for each of the three samples after exposure to the BCl_3 and evacuation. The TGA data show that the 1 : 1 complex is stable up to 400 K in each case, and that significant BCl_3 remains on each sample even above 700 K. In the case of SbF_5, the TGA data show that the coverage approaches one molecule per site at 700 K, suggesting a relatively more stable complex than that formed from BCl_3. The results also include the acetone NMR and olefin oligomerization experiments, which are used to quantify the acidity and stability of the 1 : 1 adsorption complexes.

3.1. Gravimetric and TGA results for BCl_3 and SbF_5

The data shown in figure 2a is a direct recording of the output signal from the microbalance during the exposure of the H-ZSM-5A sample to 6 Torr of BCl_3 at room temperature. The sample mass was zeroed electronically, and the uptake data has been normalized to the sample mass. The disturbance at 130 s is due to the initial introduction of the vapor to the vacuum chamber. The sample mass increased by 1100 μmol/g during the adsorption of the BCl_3 into the zeolite. The disturbance at 570 s was due to the evacuation of the balance chamber. At this point, the uptake drops to 520 μmol/g. It is important to observe that the mass uptake at this point is very nearly the same as the Brønsted acid site concentration measured with TGA of isopropylamine, shown with a dashed line. Figure 2b is the TGA data obtained after exposure of the H-ZSM-5A sample to 6 Torr of BCl_3 and evacuation at room temperature for 25 min. The data shows a slight mass loss, $\sim$ 25 μmol/g, below 400 K. At higher temperatures, the rate of mass loss is constant up to 725 K. At this temperature, 268 μmol/g of BCl_3 are still adsorbed to the zeolite, corresponding to $\sim$ 51% of the initial BCl_3.

Figure 3a is the result obtained after exposure of the H-ZSM-5B sample to 6 Torr of BCl_3 at room temperature. As with the H-ZSM-5A sample, the H-ZSM-5B adsorbs a relatively large amount of BCl_3, 880 μmol/g, during the adsorption step. When the system is evacuated at 500 s, the mass uptake drops to 373 μmol/g. Again, this mass uptake corresponds very closely to one molecule per Brønsted acid site. Figure 3b shows the TGA data obtained on heating the evacuated sample to 800 K at 10 K/min. The mass remains constant up to 400 K and the rate of mass loss is uniform with temperature up to 800 K at which point the uptake is 130 μmol/g.

Figure 4a is the data obtained using H-ZSM-5C. The uptake at 6 Torr is once again relatively high, at 800 μmol/g after 540 s, at which point the system is evacuated. The uptake under vacuum at room temperature is

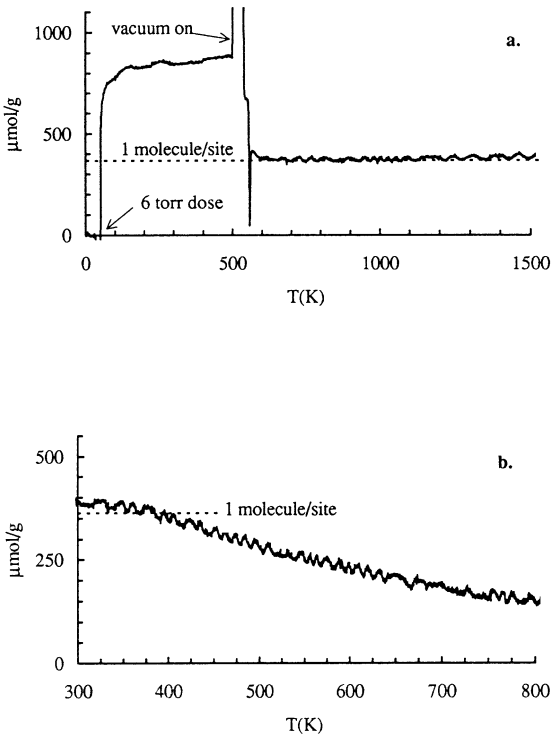


Figure 3. (a) Adsorption of BCl_3 in H-ZSM-5B. (b) TGA results for H-ZSM-5B doped with BCl_3. The heating rate was 10 K/min.

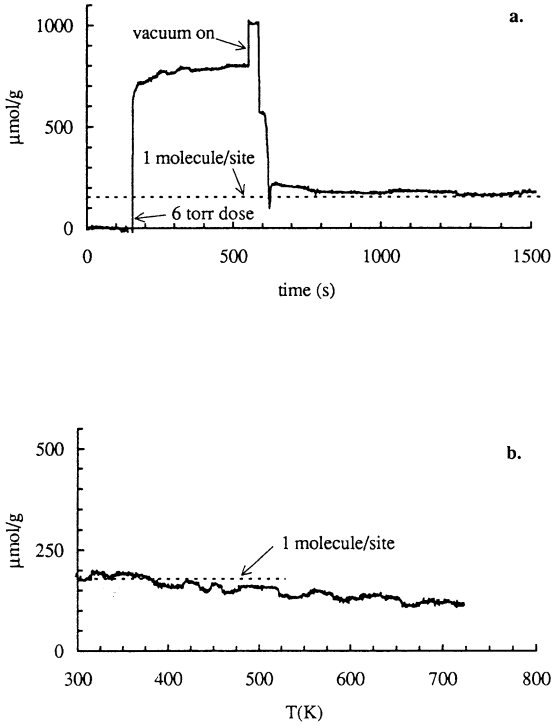


Figure 4. (a) Adsorption of BCl_3 in H-ZSM-5C. (b) TGA results for H-ZSM-5C doped with BCl_3.

225 μmol/g. This mass uptake corresponds to 1.32 molecules per Brønsted site. As with the other two samples, the TGA, figure 4b, shows a uniform rate of mass loss up to 725 K, at which point the mass uptake is 110μmol/g.

Figure 5 shows the results obtained on exposure of the H-ZSM-5A sample to 2 Torr of SbF_5 vapor at room temperature. The uptake at 2 Torr is 1380 μmol/g with respect to the clean, undosed zeolite (region B with respect to region A in figure 5). Using the QSAR calculated molecular volume of 280.77 Å^3 [26], this uptake corresponds to 0.23 cm^3/g. When compared to the ideal pore volume of 0.19 cm^3/g, this result suggests that the pores are nearly completely filled with SbF_5. On evacuation at 820 s, the sample mass remains constant, in contrast to the results shown above for BCl_3. However, on heating the sample to 700 K, we observe an uptake of 520 μmol/g, which is within experimental error of the acid site concentration of 510 μmol/g. The region of figure 5 in which the coverage of SbF_5 corresponds to one molecule per site is labelled as region C.

3.2. Acetone NMR

The acidic properties of the metal halide-treated zeolites were further investigated using ^{13}C NMR of carbonyl-labelled acetone. The chemical shift of the carbonyl carbon is influenced by the nature of the solvent [15–23]. In weak acid solvents, observed changes in the chemical shift are rationalized as being due to an increase in the deshielding of the carbonyl carbon as the strength of the hydrogen bonds with the solvent molecules is increased [15]. In very strong liquid acids where the fraction of protonated acetone molecules is significant, the observed chemical shift is the result of rapid averaging of the lines due to the protonated and unprotonated forms on the time scale of the measurement [15,27]. In zeolites, one observes a rigid complex on the time scale of the NMR measurement, and changes in the chemical shift have been assigned to hydrogen-bonding interactions between the carbonyl oxygen and the zeolite acid site [18,20,23].

Figure 6 shows CPMAS NMR spectra obtained on

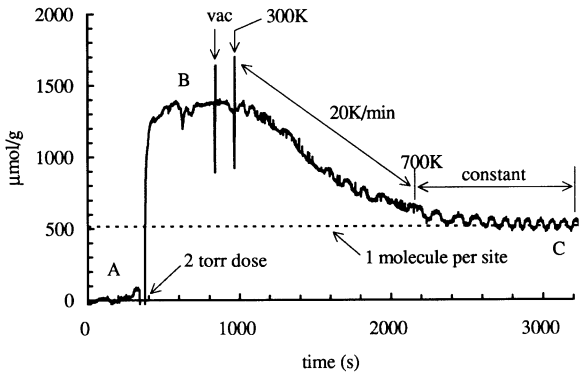


Figure 5. Adsorption and TGA of SbF_5 in H-ZSM-5A.

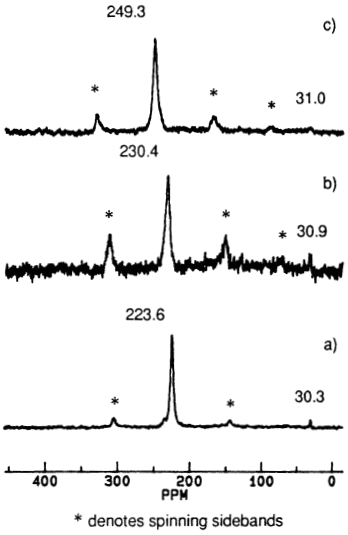


Figure 6. CPMAS NMR spectra of ^{13}C-carbonyl-labelled acetone in (a) H-ZSM-5A, (b) H-ZSM-5A saturated with SbF_5, and (c) H-ZSM-5A saturated with SbF_5 and heated to 700 K prior to exposure of acetone.

exposure of the undoped and SbF_5-treated zeolites to 0.60 molecules of acetone per zeolite Brønsted site. For acetone adsorbed on the untreated zeolite, figure 6a, we observe a single line centered at 223.6 ppm from TMS along with accompanying spinning sidebands at 304.8 and 143.8 ppm, in excellent agreement with previously published results [16–23]. The feature at 30.3 ppm is due to the natural abundance signal of the methyl carbons. We also observe a minor feature at $\sim$ 232 ppm, probably due to the presence of small amounts of nonframework Al [19,28]. Figure 6b is the result obtained on saturating the sample with SbF_5, heating to 700 K to form the 1 : 1 complex, and adsorption of acetone. The observed chemical shift is 230.4 ppm, considerably higher than that observed for acetone on pure H-ZSM-5A, figure 6a. Chemical shifts for acetone in this range have been reported for other Lewis acid systems, such as steamed HY [19,28], and ZnY [22]. Spinning sidebands are observed at 311.4, 150.8, and 74.6 ppm, and the natural abundance methyl carbon appears at 30.9 ppm. Figure 6c shows the result obtained on saturation of the zeolite with SbF_5, followed by adsorption of acetone. The observed carbonyl chemical shift is 249.3 ppm, in excellent agreement with acetone in magic acid, 249.5 ppm [30]. The figure also shows spinning sidebands at 329.8, 168.0, and 87.3 ppm, as well as methyl carbons at 31.0 ppm.

3.3. Adsorption and reaction of propene and ethene

In order to further quantify the stability of the composite materials, we investigated the polymerization reaction of propene and ethene in the SbF_5-doped and undoped H-ZSM-5A sample. Previous experiments with undoped H-ZSM-5 and H-Y have shown that the propene and ethene oligomerization reactions occur readily, with propene reacting at room temperature and ethene at slightly elevated temperatures [25,29]. At room temperature, the unreacted, physisorbed olefins are easily removed by evacuation. In contrast, the oligomers formed from propene and ethene remain adsorbed at room temperature, and cracking products are observed in desorption features in the temperature range of 400 to 550 K.

The results of our experiments are outlined in table 1. The first two experiments, runs 1 and 2, are a comparison of the propene oligomerization reaction in the undoped and SbF_5-doped H-ZSM-5A sample. We first prepared the SbF_5-saturated H-ZSM-5A sample and

Table 1
Results of the propene and ethene oligomerization experiments

Run	Sample	SbF_5 content (mass%)	Adsorbate	Saturation uptake [a] (mg/g)	Uptake in vacuum (mg/g)	Uptake at 700 K (mg/g)	Final SbF_5 content, at 700 K (mass%)
1	H-ZSM-5A	0.000	C_3H_6	101	97.4	0.000	0.000
2	SbF_5/H-ZSM-5A [b]	11.2	C_3H_6	89.3	88.6	−9.4	10.1
3	H-ZSM-5A	0.000	C_2H_4	26.3	5.6	0.000	0.000
4	H-ZSM-5A	0.000	C_2H_4	95.3 [d]	96.3	0.000	0.000
5	SbF_5/H-ZSM-5A [c]	11.9	C_2H_4	32.3 [e]	32.1	−16.4	10.1
6	SbF_5/H-ZSM-5A [f]	3.02	C_2H_4	44.9	45.8	−29.3	0.040
7	SbF_5/H-ZSM-5A [g]	14.05	C_2H_4	47.8	38.4	−60.3	7.2

[a] Mass uptake after $\sim$ 15 min on exposure to 10 Torr C_3H_6 or 45 Torr of C_2H_4.
[b] Saturated with SbF_5 and outgassed at 700 K; sample contained 514 μmol SbF_5/g zeolite.
[c] Same sample treatment as in [b], with 549 μmol SbF_5/g zeolite.
[d] Reaction initiated at 100°C.
[e] Reaction initiated at 70°C.
[f] Contained 139 μmol/g of SbF_5. Sample was dosed at room temperature and unheated prior to exposure of ethylene.
[g] Same sample treatment as in [d], with 648 μmol/g of SbF_5.

then heated the sample under vacuum to obtain the 1 : 1 complex, as discussed above and shown in figure 5. This resulted in a sample containing 11.15 mass% SbF_5, or 514 μmol/g, in good agreement with the Brønsted site concentration. On adsorption of propene, the uptake increases to 101 mg/g for the undoped zeolite, and to 89.3 mg/g for the sample containing SbF_5. On evacuation, the sample mass remains essentially constant, even on prolonged evacuation for more than 12 h at room temperature. We interpret this observation to indicate that the propene has reacted in the zeolite channels to form higher molecular weight oligomer species, as reported earlier [25,29]. The mass uptakes correspond to $\sim$ 6 and 5 propene monomers per oligomer, respectively, when calculated on a per Brønsted acid site basis. On heating at 20 K/min, these species desorb between 400 and 550 K, again in good agreement with previous results. The final mass for the undoped H-ZSM-5A after heating is identical to the initial sample mass, within experimental error. The SbF_5-doped sample does not return to its initial value and has lost 9.4 mg/g. We attribute this mass loss to desorption of some of the SbF_5 molecules. However, the sample did retain 467 μmol/g of SbF_5.

The oligomerization experiments were repeated for ethene, runs 3,4 and 5 in table 1. In the absence of heating, essentially all of the adsorbed ethene is removed on evacuation at room temperature, as shown in run 3. On heating to 373 K, run 4, the sample mass increases to 95.3 mg/g and remains constant on evacuation, indicating that reaction has occurred. This mass change is again in excellent agreement with previously published results [25,29], and corresponds to $\sim$ 7 ethene monomer units in the oligomer, on a per site basis. On heating the sample to 700 K, the sample mass returns to its initial value, indicating the absence of any residual organic material. Run 5 was conducted using the 1 : 1 SbF_5 complex, as in run 2. We note here that the reaction occurs on heating to 343 K, a slightly lower temperature than required in run 4. On heating to 700 K, the sample mass is 16.4 mg/g lower than the starting mass, corresponding to 467 μmol/g of SbF_5 that are retained by the zeolite.

The acetone NMR data presented above suggests that the thermal treatment is important in determining the acid strength of the composite material. Samples in which SbF_5 is added at room temperature and which are not heated give carbonyl shifts which are nearly identical to the magic acid, while the heated and evacuated samples produce a somewhat lower chemical shift of 230.1 ppm. We therefore investigated the stability of the SbF_5/H-ZSM-5A composite using the ethene oligomerization reaction, runs 6 and 7 in table 1. As shown by the data, reaction occurs even at room temperature. However, on heating the system to 700 K, we see that a significant amount of SbF_5 is lost from the system. Essentially all of the SbF_5 is removed in run 6, while 51.1% is lost in run 7. This result shows that while the unheated samples are more active in the ethene oligomerization reaction, they are less stable.

4. Discussion

When the BCl_3 uptakes under vacuum conditions shown in figures 2 through 4 are normalized to the sample mass and the results plotted versus the Brønsted site concentrations from figure 1, we obtain a nearly linear plot, figure 7. The experiment is reproducible, with differences in the uptake measurement on different samples of the same zeolite being less than 1%. This plot clearly shows the relationship between the amount of BCl_3 or SbF_5 adsorbed and the site concentration in the zeolite.

There has been a considerable amount of interest in the preparation and use of solid- and zeolite-supported Lewis acids [6–9,31–35]. Systems that have been studied include $AlCl_3$ in H-Y [6], SbF_5 in mixed oxides and high-Al zeolites [7], $AlCl_3$ in H-mordenite [8], BF_3 in EMT [9], and $AlCl_3$ in SiO_2 and in other solid supports including high-silica zeolites [31–35]. Our work adds significantly to this literature by showing that in acidic, silica–alumina zeolites, stable complexes of metal halides can be incorporated as 1 : 1 complexes at the Brønsted acid sites. This seems to be a general result. In addition to SbF_5 and BCl_3, we have obtained preliminary gravimetric results with BF_3, $AlCl_3$, and $SbCl_5$, showing that these species behave in a similar fashion. In the case of BF_3 we observe correlation with the acid site concentration, although the coverage is somewhat more than one molecule per site. This is probably due to interactions between the BF_3 and the silanol groups in the zeolite [31–35]. We also observe a 1 : 1 complex with $AlCl_3$ [6]. The 1 : 1 complex observed with SbF_5 is very interesting, since it appears to be stable at temperatures above 750 K, even during prolonged heating.

Makarova and co-workers used infrared spectroscopy of the hydroxyls to show that the vibrational frequency of the Brønsted hydroxyl is decreased on addition of BF_3 [9]. In that study, a structural model is

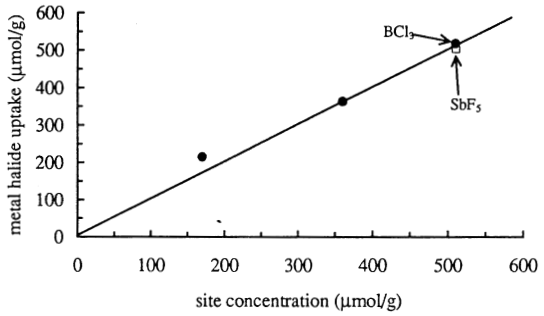
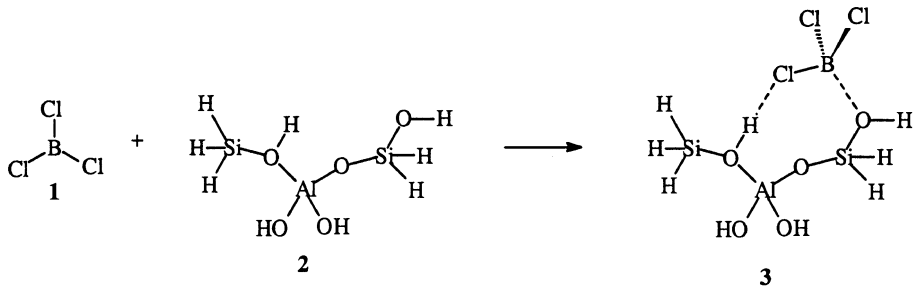


Figure 7. Plot of metal halide uptake, normalized to the sample mass, versus the Brønsted acid site concentration of the zeolite, in μmol/g.



Scheme 1.

proposed in which the BF_3 molecule is tetrahedrally coordinated at the zeolite framework Al site through interactions with the framework oxygen and the zeolite proton, as shown for the case of BCl_3 in structure **3** in scheme 1 below. The analogous BF_3 complex is energetically favorable with respect to the isolated BF_3 and zeolite site, by 233.6 kJ/mol [8]. The gravimetric data in the present study provides additional evidence that the BCl_3 molecule is forming stable complexes at the acid sites. Also, we have verified that the computational results in ref. [9] for BF_3 follow the same trend in the case of BCl_3. We view the Lewis acid, **1**, as accepting a lone pair of electrons from the zeolite site, **2**, with the "conjugate base" being stabilized by hydrogen bonding to the zeolite proton.

The present study is also interesting when viewed from the perspective of some of our previous work with ketones and aldehydes in zeolites [18–20,28]. In those studies, we showed that it is possible to produce very stable, electron-deficient carbon centers from complexes of acetone and acetaldehyde in various zeolites. At acetone coverages below one molecule per site, the acetone molecule is localized at the Brønsted site, with the carbonyl carbon significantly deshielded from that of pure acetone (223.6 ppm from TMS in the zeolite, versus 205 ppm in the liquid and 198 ppm in the gas [23]). We also showed that movement of the acetone molecule in the complex is constrained by the zeolite pore, and the degree of constraint can be changed by changing the size of the zeolite cavity [18,19]. Furthermore, by varying the acetone concentration from less than one molecule per site to more than one molecule per site, we showed that the site-localized acetone is not undergoing bimolecular collisions and therefore reactions with other acetone molecules are suppressed [20]. We feel that it is now possible to utilize some of the same "constraining" properties of the zeolite, in materials which have been doped with BF_3, BCl_3, $AlCl_3$, or SbF_5 to produce very reactive species, possibly carbocations, that are stabilized at the Lewis acid sites. For example, we have shown that acetone in SbF_5/H-ZSM-5 has a chemical shift of 249.3 ppm, compared to 249.5 ppm in magic acid.

Finally, based upon our examination of propene and ethene adsorption, we acknowledge that the stability of the zeolite/metal halide composite material is strongly dependent on the presence of large quantities of hydrocarbons, particularly at elevated temperatures and pressures. The presence of hydrocarbons and oxygenated hydrocarbons at high coverages will clearly influence the molecular dynamics and relative energetics of species adsorbed at the acid site. However, we have also shown that the stability of the metal halide at the active site depends upon the specific metal halide and zeolite combination. To map out these dependencies, we are currently characterizing various metal halide–zeolite composite materials using *n*-hexane cracking and isomerization measurements in a plug-flow reactor. These results will be the subject of future publications.

5. Conclusions

In this study we have shown that metal halide Lewis acid molecules are adsorbed by the zeolite H-ZSM-5. We have also demonstrated the presence of adsorption complexes with a stoichiometry of one molecule per Brønsted acid site. Finally, we have shown that the complexes persist in the zeolite, even at temperatures above 750 K. The results presented here have implications for the design of processes for the synthesis of various specialty chemicals as well as for the study of stable cationic intermediates in zeolites.

Acknowledgement

The authors wish to acknowledge financial support from the National Science Foundation (grant CTS-95-20920) and the Hoechst Celanese Corporation.

References

[1] G.A. Olah and A. Molnár, *Hydrocarbon Chemistry* (Wiley, New York, 1995).
[2] G.A. Olah, Angew. Chem. Int. Ed. Engl. 32 (1993) 767.
[3] G.A. Olah, Angew. Chem. Int. Ed. Engl. 12 (1973) 173.
[4] G.A. Olah, G.K. Surya Prakash and J. Sommer, *Superacids* (Wiley, New York, 1985).
[5] S. Fujiyama and T. Kasahara, Hydrocarbon Processing Int. Ed. 57 (1978) 147.

[6] T.H. Clingenpeel and A.I. Biaglow, J. Am. Chem. Soc. 119 (1997) 5077.
[7] K. Tanabe, H. Hattori and T. Yamaguchi, Crit. Rev. Surf. Chem. 90 (1990) 1.
[8] P. Wu, T. Komatsu and T. Yashima, J. Chem. Soc. Faraday Trans. 92 (1996) 861.
[9] M.A. Makarova, S.P. Bates and J. Dwyer, J. Am. Chem. Soc. 117 (1995) 11309.
[10] J.A. Phillips, M. Canagaratna, H. Goodfriend, A. Grushow, J. Almlöf and K.R. Leopold, J. Am. Chem. Soc. 117 (1995) 12549.
[11] T.J. Gricus Kofke, R.J. Gorte and W.E. Farneth, J. Catal. 114 (1988) 34.
[12] D. Parrillo, A.T. Adamo, G.T. Kokotailo and R.J. Gorte, Appl. Catal. 67 (1990) 107.
[13] W.E. Farneth and R.J. Gorte, Chem. Rev. 95 (1995) 615.
[14] L.S. Rollman and E.W. Volyocsik, Inorg. Synth. 61 (1983) 22.
[15] G.E. Maciel and J.J. Natterstad, J. Chem. Phys. 42 (1965) 2752.
[16] V. Bosacek and L. Kubelkova, Zeolites 10 (1990) 64.
[17] Z. Dolejsek, J. Novakova, V. Bosacek and L. Kubelkova, Zeolites 11 (1991) 244.
[18] A.I. Biaglow, R.J. Gorte and D. White, J. Phys. Chem. 97 (1993) 7135.
[19] A.I. Biaglow, R.J. Gorte, G.T. Kokotailo and D. White, J. Catal. 148 (1994) 779.
[20] A.I. Biaglow, J. Sepa, R.J. Gorte and D. White, J. Catal. 151 (1995) 373.
[21] T. Xu, E.J. Munson and J.F. Haw, J. Am. Chem. Soc. 116 (1994) 1962.
[22] J.F. Haw and J.B. Nicholas, in: *Studies in Surface Science and Catalysis*, Vol. 101, eds. J.W. Hightower, W.N. Delgass, E. Iglesia and A.T. Bell (Elsevier, Amsterdam, 1996) p. 573.
[23] J. Sepa, C. Lee, R.J. Gorte, D. White, E. Kassab, E.M. Evleth, H. Jessri and M. Allavena, J. Phys. Chem. 100 (1996) 18515.
[24] A.I. Biaglow, PhD Dissertation Thesis, University of Pennsylvania, USA (1993).
[25] T.J. Gricus-Kofke and R.J. Gorte, J. Catal. 115 (1989) 233.
[26] HyperChem v. 4.5, Hypercube, Inc., 419 Phillip Street, Waterloo, Ontario, Canada N2L 3X2.
[27] G.A. Olah, G.K. Surya Prakash and J. Sommer, *Superacids* (Wiley, New York, 1995) pp. 15–17.
[28] A.I. Biaglow, R.J. Gorte and D. White, J. Catal. 150 (1994) 221.
[29] A.I. Biaglow, D.J. Parrillo, G.T. Kokotailo and R.J. Gorte, J. Catal. 148 (1994) 213.
[30] G.A. Olah and A.M. White, J. Am. Chem. Soc. 90 (1968) 1884.
[31] M. Kodomari and S. Taguchi, J. Chem. Research (S) (1996) 240.
[32] S. Sato, F. Nozaki, S. Zhang and P. Cheng, Appl. Catal. A 143 (1996) 271.
[33] R.S. Drago, S.C. Petrosius and P.B. Kaufman, J. Mol. Catal. 89 (1994) 317.
[34] R.S. Drago, S.C. Petrosius and C.W. Chronister, Inorg. Chem. 33 (1994) 367.
[35] E.E. Getty and R.S. Drago, Inorg. Chem. 29 (1990) 1186, and references therein.