

Studies of Acidic Sites on Boralites by Temperature-Programmed Desorption (TPD) of NH_3 , C_2H_4 , and 1- C_4H_8

WEN-QING XU,* STEVEN L. SUIB,*†‡,¹ AND CHI-LIN O'YOUNG§¹

*Department of Chemistry, †Department of Chemical Engineering, and ‡Institute of Materials Science, University of Connecticut, Storrs, Connecticut 06269; and §Texaco, Inc., Research & Development, P.O. Box 509, Beacon, New York 12508

Received April 29, 1993; revised June 16, 1993

The acidity of [Al]-ZSM-5 is considerably strong leading to isomerization, dimerization, cracking, and coking reactions that may take place concurrently. Fine-tuning the acidity of ZSM-5 by incorporating boron into the zeolite framework is a goal of our research. From the position of boron in the periodic table, it would be expected that the substitution of aluminum with boron in the framework of pentasil zeolites would weaken the acidic strength of the zeolites. Ammonia, 1-butene, and ethylene have been used as probe molecules to study the acidic sites of zeolites. Our results show that three types of acidic sites are present on boron-containing zeolites, i.e., one inactive for reactions of 1-butene, another active for dimerization of 1-butene, and a final one responsible for isomerization of butene. Framework aluminum plays an important role in adsorption of butene or ethylene molecules on boron/aluminum ZSM-5. Butene or ethylene adsorption appears to be nonlinear with the number of acidic sites, and aluminum appears to activate the adsorption of butene or ethylene on boron acidic sites. © 1993 Academic Press, Inc.

INTRODUCTION

The acidity of zeolites can be due to Brønsted or Lewis sites. The number of acid sites, types of sites, and acid strengths are important factors that control applications of such materials in catalysis. Weak acid sites can be useful for isomerization reactions, whereas strong acid sites can lead to polymerization of reagents such as olefins (1, 2). Zeolites such as [Al]-ZSM-5 are very active for dimerization and cracking of olefins. High activity can lead to enhanced rates of coke deposition.

Incorporation of boron into the framework of zeolites can modify zeolite acidity as compared to aluminum-containing zeolites (3-8). However, the weak acidity of boron zeolites results in negligible activity for several reactions (9), such as methanol conversion to hydrocarbons, toluene alkylation with methanol, and toluene disproportionation.

In certain cases catalytic activity was linked to trace aluminum in the zeolite and not to boron sites (5, 10). On the other hand, framework substitution of boron can lead to enhanced selectivities for alcohol dehydration (5, 11), toluene alkylation (6, 12, 13), toluene disproportionation (6, 8, 14), and xylene isomerization (5, 7). The concurrent incorporation of boron and aluminum into the zeolite framework also improves shape selectivity (11).

Weakening acidity by the substitution of aluminum with boron can hopefully suppress dimerization of olefins to high molecular weight hydrocarbons and cracking to light hydrocarbons. Experiments which have been done show that boron-containing zeolites improve the isomerization selectivity to different extents. Studies of acidity and different acidic sites in boron containing pentasil zeolites are further approaches for understanding the role of framework boron in such systems.

The order of base strength for sorbates used in our temperature-programmed

¹ To whom correspondence should be addressed.

desorption (TPD) experiments is $\text{NH}_3 > 1\text{-C}_4\text{H}_8 > \text{C}_2\text{H}_4$. The secondary carbocation of C_4H_9^+ is more stable than the primary carbocation C_2H_5^+ , leading to a greater electron donation by $1\text{-C}_4\text{H}_8$ than C_2H_4 . In this paper, in addition to further studies of the synthesis and characterization (15) of boron-containing ZSM-5 zeolites, TPD of ammonia, 1-butene, and ethylene have been studied. Three types of acidic sites have been observed by using these molecules as probes. Framework aluminum plays a very important role in the acidity of such materials and appears to activate the adsorption of butene or ethylene molecules on boron acidic sites.

EXPERIMENTAL

Different concentrations of boron and aluminum in ZSM-5 and ZSM-11 samples were prepared by hydrothermal methods. Ultrapure boric acid and tetraethoxysilane were used as boron and silicon sources for preparation of aluminum-free [B]-ZSM-5, respectively. Tetrapropylamine was used as a template for the syntheses of ZSM-5 zeolites (15). Instead of ultrapure tetraethoxysilane, Ludox was used as a silicon source to prepare [B]-ZSM-5 and [B]-ZSM-11 zeolites containing low concentrations of aluminum (330 ppm). For ZSM-11, tetrabutylamine was used as a template (15). A sodium form of [B]-ZSM-5 sample containing a high concentration of aluminum (3000 ppm) was prepared with 2.7×10^{-3} wt% ultrapure boric acid, 4.6×10^{-4} wt% sodium aluminate, 15.5 wt% tetraethoxysilane, and 84.1 wt% of a 10% aqueous solution of tetrapropylammonium hydroxide. The initial pH was near 10. This precursor was then autoclaved at 190°C for 7 days. The solid product was separated by filtration, washed, dried, and calcined at 550°C for 4 h under helium and 4 h under air. The H form of this sample was prepared by ion exchange with 1 M ammonium nitrate at 80°C for 4 h followed by 4 h calcination at 550°C.

In this study, three levels of aluminum concentrations in [B]-ZSM-5 and -11 were

TABLE I
Compositions of Substituted ZSM-5 and ZSM-11 Having Different Boron and Aluminum Contents

Sample	Structure	Al (ppm)	B (ppm)	Si/(Al + B)
A	[B]-ZSM-5	0	2400	75
B1	[Al, B]-ZSM-11	330	2200	77
B2	[Al, B]-ZSM-11	330	2800	61
C1	[Al, B]-ZSM-5	330	3500	50
C2	[Al, B]-ZSM-5	330	5200	34
D	[Al, B]-ZSM-5	3000	710	58

used, one is aluminum-free [B]-ZSM-5 (sample A), others are low aluminum content [B]-ZSM-11 (samples B1 and B2) and [B]-ZSM-5 (sample C1 and C2), and the final one is high aluminum content [B]-ZSM-5 (sample D). By atomic absorption methods, the compositions of the above samples were determined and are listed in Table I. It was reported that aluminum is more readily incorporated into the framework of ZSM-5 over boron (16). Thus it is believed that aluminum is inside the framework of such zeolites.

Fourier transform infrared (FTIR) experiments were done on a Mattson GALAXY II spectrometer at a resolution of 4 cm^{-1} by using either KBr pellets or self-supporting wafers. Pyridine chemisorption experiments were done on self-supporting wafers in an *in situ* IR cell. The sample was dehydrated at 550°C for 5 h under vacuum of 10^{-5} Torr followed by adsorption of purified pyridine vapor at room temperature for 15 min. Then the system was evacuated at 150°C overnight to remove physisorbed pyridine and its infrared spectrum was recorded.

X-ray diffraction (XRD) patterns were obtained with a Scintag Model PDS 2000 diffractometer with rotary monochromatic X-ray beam and scintillator. Samples were mounted on an aluminum plate that remained horizontal during all experimentation. A beam voltage of 45 kV and a current of 40 mA were used with $\text{CuK}\alpha$ radiation.

Scanning electron microscopy (SEM) and energy dispersion X-ray (EDX) analyses

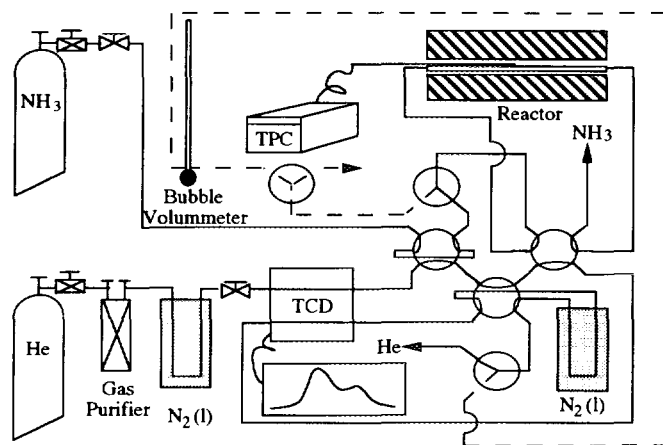


FIG. 1. Diagram of temperature-programmed desorption (TDP) apparatus.

were done on an Amray Model 1810 D microscope with an Amray PV 9800 energy dispersive X-ray analyzer which is equipped with a windowless detector so that elements with atomic numbers below Na and greater than Be can be analyzed.

The schematic diagram of a temperature-programmed desorption (TPD) apparatus is shown in Fig. 1. Ultrapure helium was purified by a Matheson gas purifier, model 6404, and further purified with a liquid-nitrogen trap. Its flowrate was 30 ml/min. Each sample (10 mg) was put into a 3/8-in (9.525-mm) diameter quartz reactor. It was pretreated by ramping from room temperature to 460°C at a rate of 15°C/min, further increasing the temperature to 500°C at 5°C/min in order to avoid temperature overshooting, holding the temperature at 500°C for 1 h, and then cooling to 100°C. A stream of adsorbate at atmospheric pressure was introduced into the adsorbent for 30 min. The system was then purged with helium for 40 min in order to eliminate physisorbed species. The TPD was followed from 100 to 610°C at a ramping rate of 15°C/min. An HP 3396 Integrator was initialized by an Omega CN 2042 temperature-programmed controller. The desorbed effluent was detected with a thermal conductivity detector. Desorption peaks were calibrated by a sample loop of known vol-

ume in order to get desorption data. For butene TPD experiments, this kind of calibration method may have a deviation of less than 4% which is estimated by the difference between the thermal conductivity of 1-butene and thermal conductivities of $(C_2H_4 + C_6H_{12})/2$ or $(C_3H_6 + C_5H_{10})/2$. Since it is difficult to analyze the TPD products (containing all kind of isomers) of 1-butene and ethylene even with a mass-spec detector, liquid-nitrogen traps were used to collect the effluent in different temperature ranges after the thermal conductivity detector. Afterwards, the trapped products were vaporized onto a column of 80/100 Carbopack coated with 0.19% picric acid and analyzed with a Varian Aerograph Series 1400 GC. Research grade ammonia, 1-butene, and ethylene from Matheson were used as adsorbates.

RESULTS

Aluminum-free [B]-ZSM-5 and different contents of boron in [B]-ZSM-5 and -11 of low aluminum content, samples A, B1, B2, C1, and C2, have been synthesized and characterized (15). For sample D, XRD patterns in Fig. 2 show that it has the ZSM-5 structure. An EDX analysis (Fig. 3) shows that this sample contains boron, oxygen, sodium, aluminium, and silicon. Figure 4

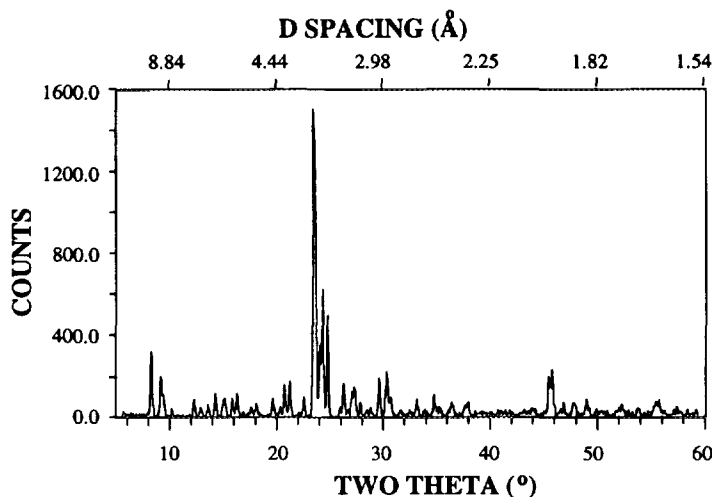


FIG. 2. The X-ray diffraction pattern of sample D.

shows infrared spectra of samples A, C2, and D. There are infrared bands at 1386, 1212, 1100, 916, 820, 559, and 449 cm^{-1} present in all these samples. Peaks of 1386 and 916 cm^{-1} are assigned to framework boron in pentasil zeolites (9, 17). The peak at 1386 cm^{-1} was further assigned to trigonal boron sites and that at 916 cm^{-1} to tetrahedral boron sites. The 916 cm^{-1} band can be used as a quantitative measurement of boron content inside the framework (17).

Pyridine adsorption experiments show

that all of the boron-containing samples have Brønsted acid sites (1547 cm^{-1}) and Lewis acid sites (1450 cm^{-1}). The peak at 1890 cm^{-1} was chosen as an internal standard to calibrate the peak area of 1547 cm^{-1} . Figure 5 shows that the area under the 1547- cm^{-1} peak due to pyridinium in Brønsted acid sites increases with combined boron and aluminum content. The ratios of Brønsted and Lewis sites are listed in Table 2.

TPD results of ammonia for these samples

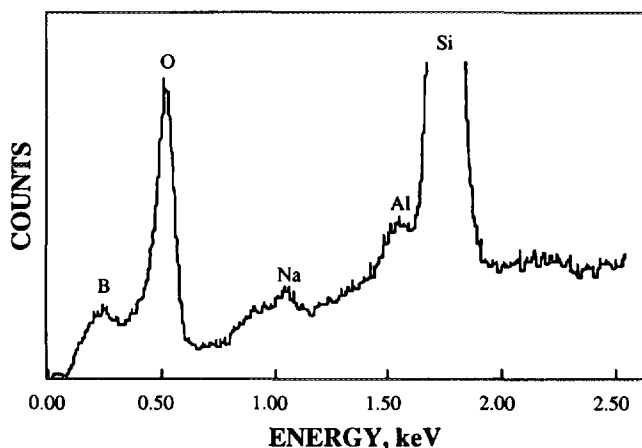


FIG. 3. Energy dispersive X-ray (EDX) analysis of sample Na-D.

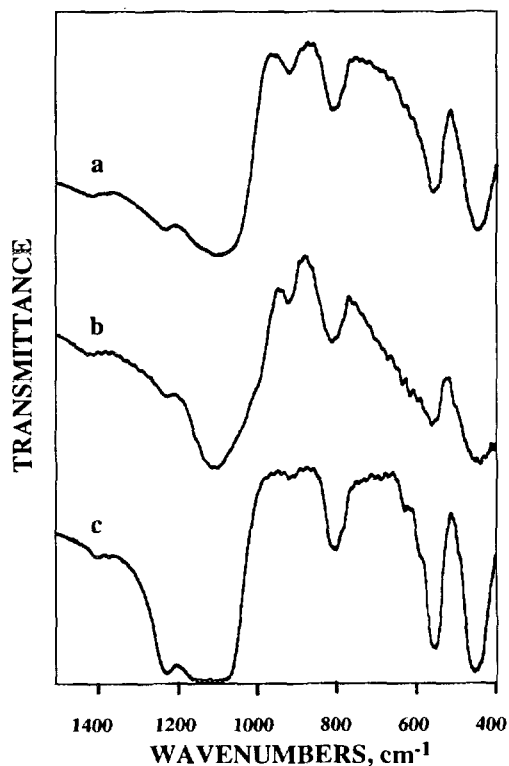


FIG. 4. Infrared spectra of (a) sample A, (b) sample C2, and (c) sample D.

are shown in Fig. 6. The results show that all of these samples have acidic sites that desorb NH₃ around 438 K, hereafter, referred to as the low temperature peak. It is obvious that sample D shows a high-temperature ammonia desorption peak at about 635 K in addition to the low temperature peak.

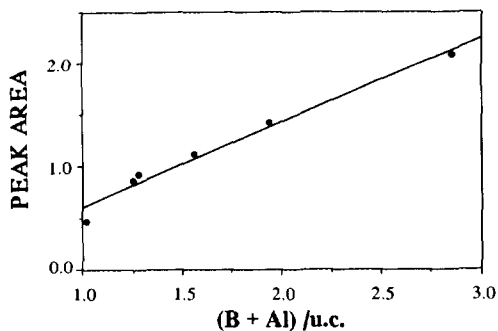


FIG. 5. Absorbance at 1547 cm⁻¹ versus B + Al Content/unit cell for boralites.

TABLE 2

Brønsted-to-Lewis Acid Ratios for Various Boralites

	Samples					
	A	B1	B2	C1	C2	D
B/L	2.49	1.10	1.14	2.56	2.86	5.93

For samples B1, B2, C1, and C2, the aluminum content is too small for the high-temperature peak to be observed.

Figure 7 shows results of 1-butene TPD over different boralites. There is no desorption peak for 1-butene over sample A or sample Na-D (sodium form of Sample D). For the B1, B2, C1, and C2 samples, the uptake of 1-butene is increased with an increase of boron content. It is obvious that ZSM-11 zeolites (B1 and B2) show one peak and ZSM-5 zeolites (C1 and C2) show two peaks. For sample D, two peaks are observed that are shifted to low temperatures.

Figure 8 shows ethylene TPD results over different boralites. In addition to sample A and sample Na-D which do not have any desorption peaks for 1-butene, B1 and B2 do not show any desorption peaks. Samples C1, C2, and D show two peaks. Comparison

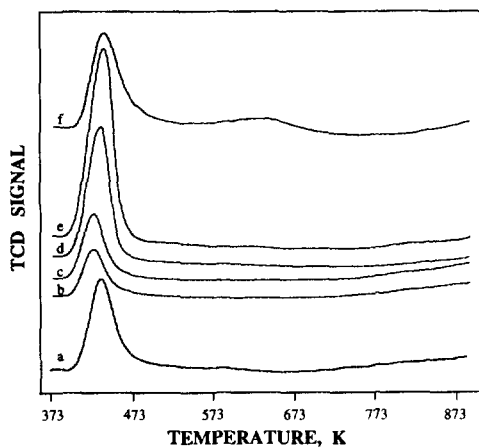


FIG. 6. TPD data for ammonia over (a) A, (b) B1, (c) B2, (d) C1, (e) C2, and (f) D.

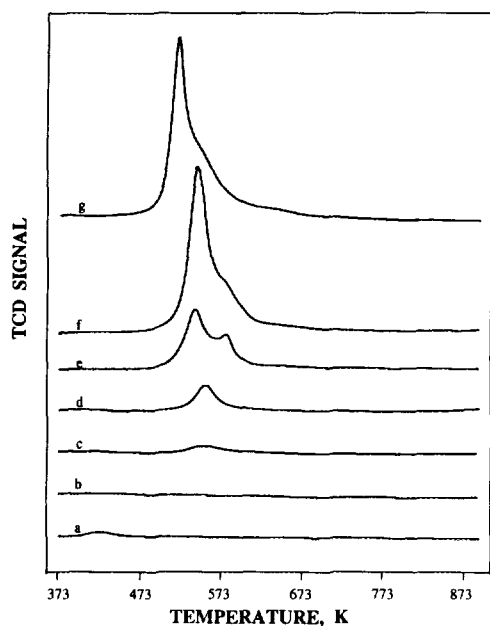


FIG. 7. TPD data for 1-butene over (a) Na-D, (b) A, (c) B1, (d) B2, (e) C1, (f) C2, and (g) D.

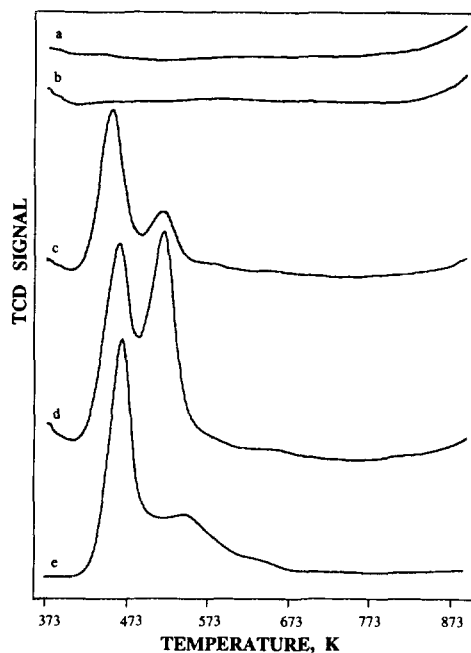


FIG. 8. TPD data for ethylene over (a) B1, (b) B2, (c) C1, (d) C2, and (e) D (signal/8).

of C1 and C2 shows that the desorption peaks of ethylene are enhanced as boron content increases.

Table 3 reports the uptakes of ammonia, ethylene, and 1-butene per unit cell of these samples. Ammonia uptake data suggest that the ammonia molecule is essentially a quantitative probe of acidic sites corresponding to the amounts of substituted framework boron and aluminum elements. However, the uptakes of 1-butene are different from one sample to another. Samples A and Na-D

do not sorb 1-butene. The uptakes of 1-butene for two ZSM-11 zeolites, B1 and B2, are less than stoichiometric in comparison to the uptakes of ammonia. For two ZSM-5 zeolites (C1 and C2) the uptakes of 1-butene are greater than stoichiometric. For high aluminum content (sample D) the uptakes of 1-butene are far greater than the stoichiometric amount of aluminum and boron. On the average, each acidic site sorbs five butene molecules which are polymerized. For the case of ethylene, samples B1 and B2 do not show any uptake in addition to A and Na-D. C1 and C2 uptake less ethylene molecules than is expected from stoichiometry. However, high aluminum content D samples have uptakes of ethylene molecules far greater than predicted by stoichiometry. These data suggest that eight ethylene molecules are polymerized on each acid site. Evidence from mass spectroscopic data suggests that products of butene reacting on sample C2 contain olefins of molecular weights such as C_{12} , C_{20} , and C_{28} .

TABLE 3

Adsorption Data of NH_3 , C_2H_4 , and $1-C_4H_8$ for Various Boralites

Sample	(B + Al)/u.c.	NH_3 /u.c.	C_2H_4 /u.c.	C_4H_8 /u.c.
A	1.28	1.30	0.00	0.00
B1	1.25	0.73	0.00	0.30
B2	1.56	1.01	0.00	0.69
C1	1.94	2.00	0.51	2.18
C2	2.85	2.99	1.17	4.37
D	1.02	1.02	8.06	5.08

Note. u.c., unit cell.

As mentioned above, no desorption peak was detected by the TCD in the butene TPD experiment for sample A or in the experiments of ethylene TPD for samples A, B1, and B2. However, liquid-nitrogen traps still can collect trace amounts of effluents which are then vaporized into a GC for analysis.

The effluents from ethylene TPD over various samples were trapped with liquid nitrogen and then were analyzed by GC methods and the results are shown in Table 4. Aluminum-free zeolite (sample A) is not able to dimerize ethylene. [B]-ZSM-5 zeolites with low aluminum content (C1 and C2) appear to contain more sites to dimerize ethylene to butene than ZSM-11 zeolite (B1 and B1). Sample C2 dimerizes more ethylene than sample C1. Sample B2 has a little more dimerization products than B1. Furthermore, high aluminum content zeolite (sample D) has an extraordinary ability to polymerize ethylene.

Figure 9 shows the product distribution of the effluents from 1-butene TPD experiments. In general, ethylene formation increases as desorption temperature increases. The formation of propylene, isobutylene, and pentene and higher olefin components all show a maximum with an increase of desorption temperature. Double bond migration of 1-butene is also enhanced as the temperature rises. The activity for 1-butene conversion for formation of propylene, isobutylene, or pentene and larger molecules has an order $A \ll B2 < C1 < D$.

TABLE 4

Product Distributions of Effluents of Ethylene TPD for Various Boralites

Species	A	B1	B2	C1	C2	D
Ethylene	100.00	98.15	97.71	96.72	91.40	14.54
Propylene	0.00	0.00	0.00	0.00	0.33	7.80
1-Butene	0.00	1.49	1.55	0.56	5.11	2.15
iso-Butylene	0.00	0.00	0.15	0.32	0.26	11.88
cis-2-Butene	0.00	0.10	0.19	0.23	0.47	4.33
trans-2-Butene	0.00	0.27	0.40	0.49	1.05	11.45
Pentene	0.00	0.00	0.00	0.90	0.62	26.00
Hexene	0.00	0.00	0.00	0.77	0.74	21.85

The maxima for propylene and pentene and higher molecular weight olefins are shifted to low temperatures as activities increase. The maxima for isobutylene formation does not shift as activity changes.

DISCUSSION

Pyridine adsorption experiments show that the boron containing pentasil zeolites all have Brønsted and Lewis acid sites. The number of Brønsted acid sites linearly increases with an increase of combined boron and aluminum content (Fig. 5). This implies that the incorporation of boron into such zeolites creates acidic sites. These boron containing samples are divided among four categories, A, B, C, and D, which have different B/L ratios. Ammonia TPD spectra in Fig. 6 further reveal differences in acidity among these boron containing pentasil zeolites. Referring to the literature (18), [Al]-ZSM-5 has a high temperature peak around 673 K. The differences of ammonia desorption temperature maxima between sample D (635 K) and [Al]-ZSM-5 (673) are obvious. Therefore, introducing boron into aluminum ZSM-5 weakens its acidity. The incorporation of boron into the framework of ZSM-5 (not containing Al) eliminates the high-temperature ammonia desorption peak. This implies that pure boralite has very weak acidity. For samples synthesized from Ludox, the aluminum content is too small (330 ppm) for the high temperature peak to be observed. Thus it is concluded that the higher the aluminum content, the stronger the acidity.

From 1-butene TPD results (Fig. 7), it is clear that aluminum free [B]-ZSM-5 and Na[Al, B]-ZSM-5 do not have any desorption peaks. This suggests that the acid sites are responsible for the adsorption of 1-butene and that acid sites on aluminum free zeolites are too weak to adsorb 1-butene. However, the uptake of 1-butene is increased with an increase of boron content in aluminum-containing [B]-ZSM-5 and [B]-ZSM-11. When the aluminum content is increased to 3000 ppm, the uptake of 1-

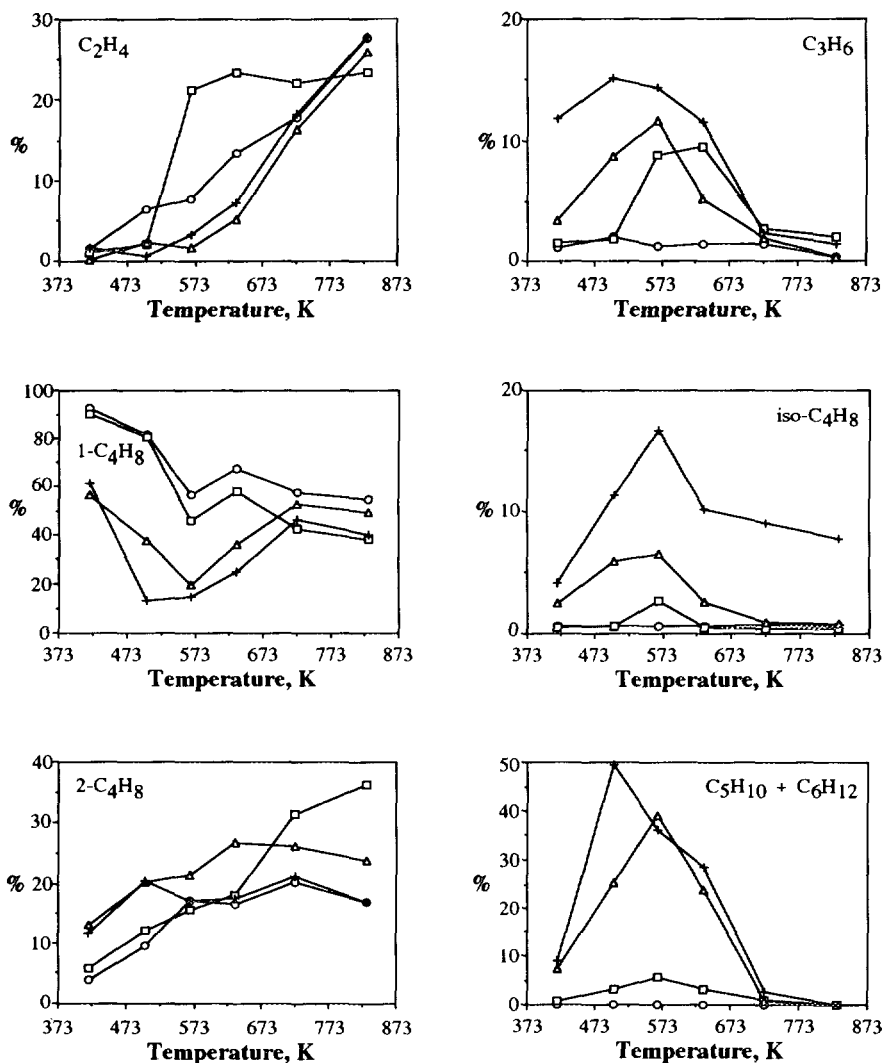


FIG. 9. Product distribution of effluents of 1-butene TPD: (○) A, (□) B2, (△) C1, and (+) D.

butene molecules is far greater than the actual number of acid sites. Ethylene TPD data showed that two aluminum-containing [B]-ZSM-11 zeolites do not uptake ethylene in addition to aluminum free [B]-ZSM-5 and Na[Al, B]-ZSM-5. For aluminum-containing [B]-ZSM-5 zeolites, the uptake of ethylene is increased with increase of boron content. Thus, it is concluded that the acid strength of ZSM-11 is weaker than ZSM-5 for B1, B2, C1, and C2. From the above results, three kinds of adsorption sites are

believed to exist on these boronites, as depicted in Fig. 10.

Ammonia probes all acidic sites. Part of these sites cannot be probed by 1-butene. Among the sites which are active for 1-butene, part of these sites are active for ethylene molecules. All these results also show that aluminum plays a very important role in the adsorption of 1-butene and ethylene. Framework aluminum appears to activate boron sites to adsorb butene or ethylene molecules. These data may also imply that

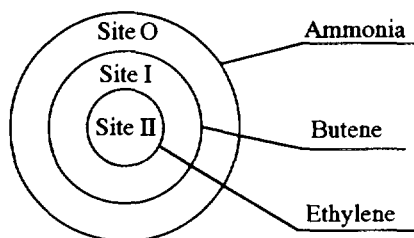


FIG. 10. Classification of acid sites probed by ammonia, 1-butene, and ethylene. Site O, adsorption of ammonia; site I, adsorption of ammonia and butene; and site II, adsorption of ammonia, butene, and ethylene.

ethylene or 1-butene first adsorb onto acidic framework aluminum sites and then adsorbed species are rearranged inside a zeolite cage and are adsorbed on boron sites. In the absence of aluminum, the adsorption of butene or ethylene is negligible. The above suggestions are also supported by the fact that a synergistic effect between boron and aluminum (5–8, 11–14) was also observed in pentasil zeolites for butene isomerization (19).

Different patterns for ethylene, 2-butenes, and propylene, isobutylene, or pentene and higher molecular weight olefins in Fig. 9 suggest that ethylene and 2-butenes are not produced at the same sites as those used to form propylene, isobutylene, or pentene. It is difficult to find a way to exactly correlate data for ethylene and 2-butenes with corresponding acidic properties.

As discussed above, the higher the boron content, the greater the number of acidic sites. A higher density of acidic sites will favor dimerization of ethylene. The higher content of aluminum, the stronger acid sites on the boralite with concomitant enhanced dimerization of ethylene molecules. These also would lead to a higher activity for 1-butene conversion. The data of Table 4 for ethylene TPD and Fig. 9 for 1-butene TPD are understandable in this context. Furthermore, if butene molecules are dimerized, stronger acidity will lead to cracking at lower temperature when desorption temperature increases. Thus it can be seen that the temperature maxima for the formation

of propylene and pentene and higher molecular weight species are shifted to low temperature with an increase of acid strength. Skeletal isomerization may take place on sites different from those active for the dimerization since temperature maxima for isobutylene formation do not shift.

The activity for 1-butene conversion on these boralites may be related to the Brønsted/Lewis ratio. The higher the ratio of Brønsted to Lewis sites, the more active the catalyst ($D > C1 > B2$). Boralite A is inactive even though its B/L ratio is in between those of C1 and B2 since acidic framework boron sites are not able to adsorb 1-butene molecules without the presence of aluminum.

For purpose of clarity in the discussion, there are three types of acidic sites, site O, site I, and site II, as diagrammed in Fig. 10. Site II adsorbs ammonia, butene, and ethylene, site I adsorbs ammonia and butene but not ethylene, and site O only adsorbs ammonia but not butene or ethylene. The amount of site O for sample A is equal to the amount of ammonia uptake (1.3 sites/u.c.) since it does not adsorb butene and ethylene. Since not much dimerization occurred on sample B2 (Fig. 9), this suggests that each site adsorbs only one butene molecule which is one of our assumptions. The difference between ammonia uptake and 1-butene uptakes (amounts of Site O) are 0.43 site/u.c. for B1 and 0.32 site/u.c. for B2 (Table 3) which are inactive for the adsorption of 1-butene. It seems that there is no site O for samples C1 and C2 since the butene uptakes are greater than ammonia uptakes. From Table 4, the dimerization of ethylene for samples B and C is not significant. Thus it is believed that ethylene molecules can probe one kind of acid site (site II). A reviewer has suggested that the adsorption amount on site I for samples C1 and C2 can be calculated as follows (refer to Table 5):

$$M = \Sigma - S. \quad (1)$$

On site II, the amount of adsorbed butene

TABLE 5

Calculated Amounts of Butene Adsorbed on Three Sites on C1 and C2 (unit = site/u.c.)

Sample	Σ	S	M	B_T	B_S	B_S/S
C1	2.00	0.51	1.49	2.18	0.59	1.4
C2	2.99	1.17	1.82	4.37	2.55	2.2

Note. It is assumed that one butene is adsorbed per moderate strength site (site I). Σ , total amount of sites (ammonia uptake); S , amount of strong sites (ethylene uptake, site II); M , amount of moderate sites (site I); B_T , total amount of butene uptake; B_S , amount of butene adsorbed on strong sites.

is equal to the total uptake of 1-butene minus that of the amount of site I,

$$B_S = B_T - M \quad (2)$$

The number of butene molecules dimerized on site II, B_S/S , can then be calculated. The B_S/S values for C1 and C2 (Table 5) which are significantly greater than one suggest that site II is responsible for the dimerization of butene molecules. Since the basic strength for ethylene is weakest among ethylene, 1-butene, and ammonia, the acidity of the sites probed by ethylene is strongest. Thus it seems that the sites probed by ethylene (site II) are responsible for the dimerization of butene molecules. The basic strength of 1-butene is of intermediate strength as compared to ethylene and ammonia. Therefore, the sites probed by 1-butene (site I) are moderately acidic and it suggested that such sites are responsible for the adsorption of 1-butene and its isomerization. Site O probed by ammonia (a strong base) is the weakest acidic site and is inactive for reactions of 1-butene.

As discussed above, the higher the density of acidic sites, the greater the chance of dimerization of butene. This model also explains why the low boron content B1 has more sites (0.43 site/u.c.) that are inactive for butene than the high boron content sample B2 (0.32 site/u.c.). It also explains why the high boron content sample C2 can dimer-

ize more butene molecules (2.2) than C1 (1.4).

During preparation of this paper, Basini *et al.* (20) published a paper concerning FTIR studies of NH_3 on [B]-ZSM-5 zeolites. Basini *et al.* (20) conclude that three types of NH_3 sorption sites exist on these materials. Our results for NH_3 , C_2H_4 and 1- C_4H_8 sorption also imply the presence of three types of sites on borolites and are entirely consistent with results of Basini *et al.* (20).

CONCLUSIONS

A hybrid [Al, B]-ZSM-5 zeolite has been synthesized and characterized. Introduction of boron into the framework of [Al]-ZSM-5 weakens its acidity. With an increase of aluminum content, the acid strength is increased. The acidity of pure [B]-ZSM-5 is too weak for reaction of 1-butene or ethylene. The presence of aluminum in the framework is very important for 1-butene or ethylene adsorption or boron sites. The adsorbed intermediates may be rearranged inside zeolite cages. Aluminum appears to activate boron sites that adsorb butene and ethylene molecules. With an increase in the density of acidic sites, the ability to dimerize 1-butene or ethylene is increased. Meanwhile, a high aluminum content significantly enhances the dimerization of ethylene or butene. There are at least three kinds of acid sites in these materials, one site is inactive for olefins, one catalyzes dimerization of olefins, and the other is responsible for isomerization of *n*-butene.

ACKNOWLEDGMENTS

The authors thank Texaco, Inc., and the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, for their support of this research. The authors also thank Dr. Sang Sung Nam for preparing aluminum-free [B]-ZSM-5.

REFERENCES

1. Szabo, J., Perrotey, J., Szabo, G., Duchet, J. C., and Cornet, D., *J. Mol. Catal.* **67**, 79 (1991).
2. Choudhary, V. R., *Chem. Ind. Dev.*, 32 (1974).
3. Scholle, K. F. M. J. G., Kentgens, A. P. M., Vee-man, W. S., Frenken, P. F., and Ven der Velden, G. P. M., *J. Phys. Chem.* **88**, 5 (1984).

4. Kofke, T. J. G., Gorte, R. J., and Kokotailo, G. T., *J. Catal.* **116**, 252 (1989).
5. Chu, C. T.-W., Kuehl, G. H., Lago, R. M., and Chang, C. D., *J. Catal.* **93**, 451 (1985).
6. Sayed, M. B., Aroux, A., and Vedrine, J. C., *J. Catal.* **116**, 1 (1989).
7. Kutz, N. A., in "Perspectives in Molecular Sieve Science" (W. H. Flank and T. E. Whyte, Eds.), ACS Symposium Series, Vol. 368, p. 532. ACS, Washington, DC, 1988.
8. Beyer, H. K., and Borbely, G., in "Proc. 7th Int. Zeolite Conf." (Y. Murakami, Ed.), p. 867. Elsevier, Amsterdam, 1986.
9. Coudurier, G., and Vedrine, J. C., *Pure Appl. Chem.* **58**, 1389 (1986).
10. Gaffney, T. R., Pierantozzi, and Seger, M. R., in "Zeolite Synthesis" (M. L. Occelli and H. E. Robson, Eds.), ACS Symposium Series, Vol. 398, p. 374. ACS, Washington, DC, 1989.
11. Howden, M. G., *Zeolites* **5**, 334 (1985).
12. Taramasso, M., Perego, G., and Notari, B., in Proc. 5th Int. Conf. on Zeolites, 1980, p. 40.
13. Coudurier, G., Auroux, A., Vedrine, J. C., Farlee, R. D., Abrams, L., and Shannon, R. D., *J. Catal.* **108**, 1 (1987).
14. Auroux, A., Sayed, M. B., and Vedrine, J. C., *Thermochim. Acta* **93**, 557 (1985).
15. Simon, M. W., Nam, S. S., Xu, W.-Q., Suib, S. L., Edwards, J. C., and O'Young, C.-L., *J. Phys. Chem.* **96**, 6381 (1992).
16. Barrer, R. M., (Ed.), "Hydrothermal Chemistry of Zeolites", p. 284. Academic Press, London, 1982.
17. Jansan, J. C., de Ruiter, R., Biron, E., and van Bekkum, H., in "Zeolite: Facts, Figures, and Future" (P. A. Jacobs and R. A. van Santen, Ed.) p. 679. Elsevier, Amsterdam, 1989.
18. Hunger, B., Hoffmann, J., Heitzsh, O., and Hunger, M. *J. Thermo. Anal.* **36**, 1379 (1990).
19. Bianchi, D., Simon, M. W., Nam, S. S., Xu, W.-Q., Suib, S. S., and O'Young, C.-L., submitted for publication.
20. Basini, L., Cornaro, U., and Aragno, A., *Langmuir* **8**, 2172 (1992).