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The Acidity and Catalytic Activity of Alumino- and Borosilicate Pentasil Zeolites: A Comparison

Isomorphous substitution of B^{3+} for Al^{3+} in pentasil zeolite framework has been reported recently (*1–8*). The presence of boron in tetrahedral lattice sites has been confirmed by solid state NMR (*3, 5, 7*) and X-ray (*1, 2*) data. Compared to the aluminosilicate, HZSM-5, these borosilicate analogs (borolites) have been found to be more selective for the production of light olefins (ethylene, propylene and butenes) from methanol (*2, 3*). Since the conversion of methanol to dimethyl ether and further to light olefins occurs on acidic sites (*9*), it is logical to expect that the observed differences in the catalytic behavior of HZSM-5 and H-borolites arise from differences in the acidity and acid strength distribution in these two systems. By means of proton magic angle spinning NMR and NH_3-TPD experiments Scholle *et al.* (*10*) found that the acidity decreases on going from Si—OH—Al, the Brønsted acidic sites in HZSM-5 to Si—OH—B, the Brønsted acid sites in H-borolite, to Si—OH, the terminal silanol group of the zeolite lattice. The present note compares the acid strength distribution (as revealed by the temperature-programmed desorption (TPD) of NH_3) and catalytic activity (in the conversion of methanol to hydrocarbons) of HZSM-5 and H-borolite. It is shown how differences in acidity can account for the higher production of light olefins over H-borolite.

HZSM-5 (sample 1) was prepared as reported earlier (*11*). Sample 2 was prepared by heating sample 1 at 873 K for 4 hr in a flow of steam. Sample 3 was obtained by refluxing sample 2 in 0.2 *N* HCl for 8 hr, filtering, washing, and drying at 393 K. Sample 4 was a H-borolite (*3*). The presence of boron in the framework was confirmed by NMR (*3*). Samples 5 and 6 were prepared from sample 4 by procedures similar to those used in the preparation of samples 2 and 3, respectively. Samples 7–9 were H-borolites with SiO_2/B_2O_3 ratios of 86, 200, and 600, respectively. Sample 10 was silicalite (*11*). All the samples were calcined at 723 K in dry air for 6 hr. The chemical composition of the samples, determined by atomic absorption is given in Table 1. All the samples were highly crystalline. The residual aluminum content in samples 4–9 (borolites) arising out of the Al impurity present in the sodium silicate raw material was estimated by neutron activation analysis. The values were 72, 70, 65, 63, 68, and 66 ppm, respectively. While it is recognized that in pentasil zeolites small amount of Al in tetrahedral framework positions can have measurable catalytic activity, we feel that the broad conclusions regarding the relative acid strength and catalytic activity of alumino- and borosilicate pentasil zeolites made in this paper will still be valid even though the magnitude of the difference might vary. The TPD of NH_3 and measurement of the catalytic activity were done as described in earlier publications (*12, 13*).

ACIDITY

Figure 1 illustrates the TPD of NH_3 from all the samples. In the case of samples 1–3 (HZSM-5), three peaks centered at 373, 473, and 723–773 K are seen. This is in agreement with Topsoe *et al.* (*14*), who have reported data on TPD of NH_3 from HZSM-5. Three distinct peaks (333–373,

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TABLE 1

Chemical Composition of Samples 1–10

No.	Sample	Unit cell composition
1	AlHZSM-5	$Na_{0.31}H_{4.95}[(SiO_2)_{90.74}(AlO_2)_{5.25}]$ 29.5 H_2O
2	AlHZSM-5 (ST)	$Na_{0.35}H_{4.95}[(SiO_2)_{90.74}(AlO_2)_{5.25}]$ 20.2 H_2O
3	DAlHZSM-5	$Na_{0.1}H_{3.8}[(SiO_2)_{92.0}(AlO_2)_{4.0}]$ 19.6 H_2O
4	HBOR-1	$Na_{0.39}H_{4.80}[(SiO_2)_{90.74}(BO_2)_{5.25}]$ 21.0 H_2O
5	HBOR-1 (ST)	$Na_{0.39}H_{4.80}[(SiO_2)_{90.74}(BO_2)_{5.25}]$ 18.0 H_2O
6	DHBOR-1	$Na_{0.15}H_{3.0}[(SiO_2)_{92.8}(BO_2)_{3.2}]$ 15.0 H_2O
7	HBOR-2	$Na_{0.3}H_{1.87}[(SiO_2)_{93.83}(BO_2)_{2.17}]$ 16.2 H_2O
8	HBOR-3	$Na_{0.28}H_{0.68}[(SiO_2)_{95.07}(BO_2)_{0.96}]$ 15.5 H_2O
9	HBOR-4	$Na_{0.2}H_{0.18}[(SiO_2)_{95.62}(BO_2)_{0.35}]$ 14.0 H_2O
10	Silicalite	$Na_{0.05}H_{0.15}[(SiO_2)_{95.76}(AlO_2)_{0.2}]$ 12.0 H_2O

423–473, and 693–773 K, respectively) were observed of which the high temperature one correlated with the Na content. Haag *et al.* (*15*) have recently pointed out that the three desorption maxima usually observed in NH_3-TPD spectra of HZSM-5 do not necessarily indicate the presence of three different types of acid sites but are rather indicative only of the presence of NH_3 in three different "energy states." Catalytic activity in the cracking of paraffins correlated well with the concentration of tetrahedral Al^{3+} ions and the associated Brønsted acid sites (*15*). Similar, linear correlations between the concentration of strong acid sites (responsible for the NH_3 TPD maximum at 700–773 K) and catalytic activity was also inferred by Babu *et al.* (*12*) and Borade *et al.* (*16*) in the isomerization of *o*-xylene and cracking of *n*-hexane, respectively. Apparently, only the acid sites responsible for the high temperature maximum (700–773 K) in the TPD spectra of NH_3 are sufficiently acidic to protonate hydrocarbons and catalyse their further transformation. The other two maxima at 373 and 473 K in the TPD spectra are associated with weaker acid sites which can protonate/chemisorb a relatively strong base like NH_3 but are too weakly acidic to protonate weaker bases like hydrocarbons. It is likely that the Brønsted acid site associated with the tetrahedral framework Al^{3+} ion is responsible for the 700–773 peak in the TPD spectra. The peaks at 373 and 473 K are probably associated with silanol groups (*17*) which are not associated with tetrahedral framework Al^{3+} ions.

The major differences observed in the TPD spectra on isomorphous substitution of B^{3+} for Al^{3+} (curves 4–9 in Fig. 1) are

(1) the negligible intensity of the high temperature peak at 723–773 K in the H-borolites in contrast to its significant presence in HZSM-5, and

(2) the presence of a TPD peak at 573–623 K in borolites and its absence in HZSM-5. The absence of the high temperature peak in borolites as well as silicalite (sample 10, curve 10 of Fig. 1) had also been reported earlier by Scholle *et al.* (*10*).

It is concluded that in contrast to HZSM-5, H-borolites do not contain strong acid sites. Moreover, the desorption of a significant amount of NH_3 in the intermediate 573–623 K region (especially in samples 4 and 5, see Fig. 1) reveal that important differences exist in the type and concentration of even weakly bound NH_3 molecules between HZSM-5 and H-borolites. A possible consequence of this feature on the catalytic property of the borolites is discussed later. The intensity of this peak at 573–623 K is negligible at higher values of SiO_2/B_2O_3 (samples 7–9).

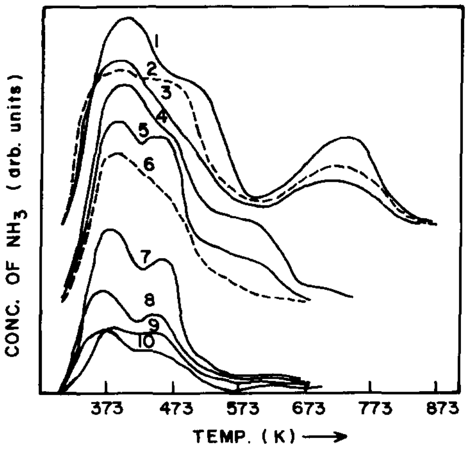

FIG. 1. TPD spectra of NH_3 from samples 1–10.

TABLE 2

Methanol Conversion on Aluminosilicate and Borosilicate Zeolites

Sample	1(Al)	2(Al)	3(Al)	4(B)	5(B)	6(B)	7(B)	8(B)	9(B)	10(Si)
Methanol conversion (wt%)	96	99	99	98	97.4	98.74	99.4	100	95.2	100
Dimethyl ether (wt%)	2.3	0.4	0.3	0.4	1.46	—	—	—	3.4	—
Hydrocrabons (wt%)										
Ethylene	20.2	12.4	23.7	21.7	15.97	19.22	15.99	18.84	15.24	14.84
Propyene	20.9	14.20	26.1	39.6	36.80	42.73	29.93	35.02	29.90	24.61
Butenes	4.4	2.4	5.6	17.5	12.88	14.60	12.37	11.77	14.96	10.85
Methane	6.8	7.5	5.6	2.3	2.37	3.55	4.72	2.73	8.8	8.50
Ethane	0.2	2.0	1.2	Traces	Traces	0.78	1.40	—	1.1	
Propane	5.9	8.3	2.4	2.8	1.47	1.99	0.20	1.59	0.69	11.06
Butanes	10.4	10.5	3.5	0.7	1.81	1.59	0.70	1.08	0.49	
C_5^+	29.2	42.2	31.0	15.4	29.62	15.54	33.96	28.22	29.41	30.13

Note. Feed = 80% methanol in water (wt%), WHSV = 2.5 hr^{-1}, temp. = 823 K.

CATALYTIC ACTIVITY

The product distribution in the conversion of methanol over samples 1–10 is shown in Table 2. The results obtained when Al^{3+} is replaced by B^{3+} in the pentasil lattice may be summarized as follows: (1) the concentrations of propylene and butene are enhanced, while (2) those of light paraffins like propane and butane are suppressed; (3) the concentration of aromatics in the C_5^+ product was much lower over borolites than in the case of the aluminium analogs; (4) extraction with mineral acid (leading to dealumination/deboration of surface and extra lattice Al or B species, respectively) enhances the selectivity for light olefins (compare samples 2 and 3 (for Al) and 5 and 6 (for B), respectively).

In the conversion of methanol to hydrocarbons, the light olefins are key intermediates which react further through alkylation, disproportionation, and oligomerization reactions to yield C_5^+ products. Possible ways of enhancing the yield of light olefins include (1) the suppression of those acid sites which catalyze the further reactions of light olefins and (2) the enhancement of the "constraint index" of the zeolite pores so that either the bulkier C_5^+ products are not formed at all or even if they are formed, they undergo secondary cracking to lighter olefinic products due to their longer residence time inside the constrained pores of the zeolites. Both these factors are probably responsible for the higher formation of light olefins over the borolites. As mentioned earlier, a significant difference between the TPD spectra of Al and B zeolites is the absence of the high temperature peak at 700–773 K and the presence of a new peak at 573 in the latter. The peak at 573 K [observed at 523 K by Scholle *et al.* (*10*)] is probably related to the presence of Si—OH—B Brønsted acid sites which are weaker than the Si—OH—Al sites (*10*). While these sites are acidic enough to catalyze the formation of light olefins by dehydration and alkylation reactions, they are, perhaps, not sufficiently acidic to catalyze their further disproportionation and oligomerization to yield C_5^+ products. The catalytic activity of sample 10 (silicalite) is due to the presence of Al^{3+} impurities in it.

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