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The Effect of Modification with Boron on the Catalytic Activity and Selectivity of HZSM-5

I. Impregnation with Boric Acid

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The characterization of the boron modifier and its role in modifying catalytic processes on HZSM-5 have been studied. Investigation by infrared (IR) spectroscopy of the modified zeolite reveals that boron is present in the form of boric anhydride linked to the zeolite framework via condensation with a Brønsted site. This is indicated by two spectral aspects: (i) evidence of the borosilicate $=B-O-Si\equiv$ grouping (band at ca. 930 cm^{-1}) and (ii) a linear decrease in Brønsted site band absorbance (population) at ca. 3610 cm^{-1} with increased boron content of the zeolite. Evidence by this technique, supported by X-ray diffraction, indicates that boron has no effect on the zeolite structure. Thermogravimetric (TG) data from *n*-hexane and 3-methylpentane sorption indicate that the adsorption kinetics of the latter adsorbate and the maximum sorption capacity of both adsorbates fall with increasing boron content of the zeolite. Agreement between both techniques (IR and TG) indicates that while boron locates totally within the zeolite grain for the low boron content samples, it locates partly within the grain and partly on the external surface for the high boron content sample. Also, agreement between calculation and experimental findings indicates that a maximum of ca. 5–6 boron atoms per zeolite unit cell can be accommodated within the grain. The effect of boron impregnation on the catalytic activity and selectivity of the zeolite has been studied as a function of time for both toluene alkylation (with methanol) and disproportionation. Initial reactivity is high for all samples but falls with time, varying with boron content. Selectivity to *p*-xylene also varies with time in a nonregular way, indicating boron mobility within the zeolite grain. The distribution of xylene products in both toluene alkylation and disproportionation reveals that different mechanisms are governing their formation within HZSM-5. © 1986 Academic Press, Inc.

INTRODUCTION

Shape-selectivity in zeolite chemistry has received much attention and increasing interest since the pioneer work of Weisz and Frilette (*1*) in 1960. In the following decade, the subject was reviewed by Chen and Weisz (*2*) and by Venuto (*3*). With the discovery of the new pentasil zeolite, ZSM-5 (*4*), more interest has been given to shape-selectivity, science, and technology. Recently Csicsery (*5*) has provided a review with discussion for the most important features affecting shape-selectivity in zeolite chemistry. Several reviews (*6–9*) have appeared with critical discussion for the parameters governing shape-selectivity and catalysis for different zeolites. The shape-selectivity peculiar to ZSM-5 has been attributed to its unique structure, which has been described by Kokotailo *et al.* (*10*).

One of the important shape-selectivity-based catalytic processes is the production of xylenes rich in the *p*-isomer. ZSM-5, in spite of its unique structure, has usually yielded xylenes near the thermodynamic equilibrium distribution. This has been observed for methanol to gasoline conversion and toluene disproportionation more than for toluene alkylation by methanol. This has been attributed to different reaction pathways. In a number of patents and scientific papers, it appears that certain treatments (*11–19*) (during or after the zeolite synthesis) are effective in modifying ZSM-5 shape-selectivity. This has

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been mainly achieved by increasing the internal surface (enlarging the zeolite crystal), decreasing the external surface (by either coating or terminating the zeolite crystal with Al-free surface), and partly blocking the channel structure with inorganic filler. This modification has been generally exploited in producing products rich in the more valuable isomers, particularly in the production of xylenes rich in *p*-xylene. It has been possible to produce *p*-xylene with percentages exceeding the thermodynamic equilibrium (*20*) to higher than 90%. Recently, the factors governing shape-selectivity in xylene isomerization and toluene disproportionation over ZSM-5 have been discussed by Olson and Haag (*21*).

The series of studies by Kaeding *et al.* (*16–19*) has highlighted certain key points regarding the role of the modifier in improving the zeolite selectivity. The aim of the present investigation was to find a model capable of explaining and relating modified catalytic behaviour to the modifier. The role of boron in modifying ZSM-5 activity and selectivity for both toluene alkylation (by methanol) and disproportionation has been investigated with time. This was to add more insight to the understanding of the role of the modifier in such catalytic processes.

EXPERIMENTAL

Materials

The starting ZSM-5 sample was synthetised, as previously described (*22*), in an autoclave at 443 K for 5 days. From this parent NH_4NO_3-acidified ZSM-5, three other samples were prepared following Ref. (*16*) by impregnating 2 g of the H-ZSM-5 with different amounts of aqueous boric acid solution. After impregnation under vigorous stirring at 348 K for 17 h the mother liquor was decanted to avoid as much as possible the presence of boron on the external surface of the zeolite grains. The solids were then dried at 393 K and calcined in flowing air for 16 h at 773 K. The bulk chemical analysis of the samples are given in Table 1. Note that no change in Na + K and Al contents were observed.

A silicalite-type sample was prepared in the same way, obviously without any Al source except for Al impurities in the starting silica.

High-purity grade methanol and toluene (Merck) were used as reactants.

Equipment and Methods

Infrared spectroscopy. Samples of ca. 14 mg were pressed under low pressures (20 kg cm^{-2}) into self-supporting wafers (ca. 5 mg cm^{-2}). The wafers were degassed under vacuum (0.133 mPa) at increasing temperatures up to 673 K, with the latter temperature being kept constant for 2 h. The wafers were then cooled to 293 K, and the IR spectra of the zeolite were recorded using a double-beam Perkin–Elmer spectrometer Series 580, with resolution of ca. 2.8 cm^{-1}. Highly absorbing vibrations (e.g., lattice vibrations) were determined by diluting the samples (1 wt%) in KBr disks without further pretreatment.

Thermogravimetry and adsorption kinetics. Samples of ca. 25 mg were treated under vacuum (0.133 mPa). Temperature rise was programmed (3 K min^{-1}) to 673 K, with the latter being kept constant for at least 2 h. The samples were then allowed to cool down to 293 K, where the adsorption of both *n*-hexane and 3-methylpentane was carried out in different sets of experiments. The adsorption of the latter adsorbate was preferentially followed by kinetics using a Sartorius thermobalance. For obtaining accurate comparison of kinetics, equal amounts of the zeolite were exposed to the same sorbate pressure (400 Pa) at the same temperature (293 K). The maximum sorption capacity under these conditions was usually measured after prolonged adsorption (ca. 16 h).

Catalytic reactions. Both toluene alkylation and disproportionation reactions were studied using a flow microreactor with online gas chromatograph (GC). A fixed bed containing 50-mg samples was used. The

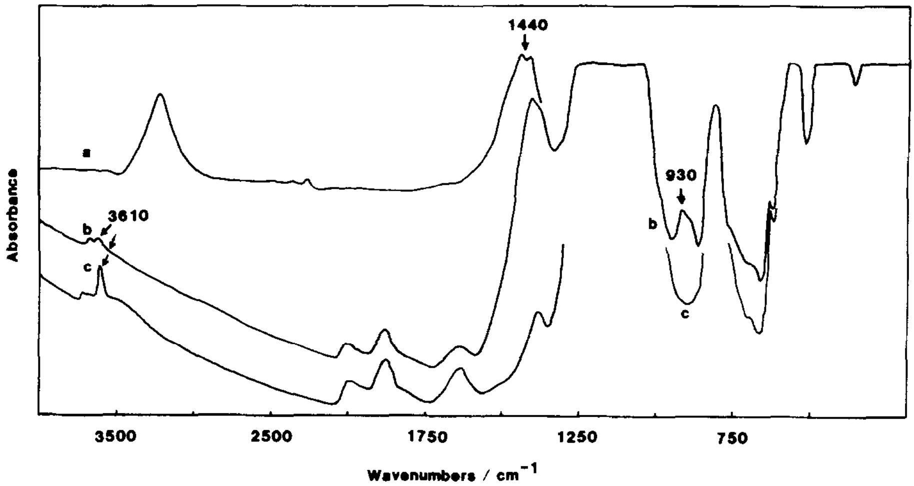


FIG. 1. Infrared spectra (4000–200 cm^{-1}) of unmodified and modified boron/HZSM-5. (a) The result of spectral subtraction for nondegassed HZSM$_3$-5 − HZSM$_0$-5. This is essentially the boric acid spectrum. (b) HZSM$_3$-5 after degassing (0.133 mPa) at 673 K for 2 h. (c) HZSM$_0$-5 after degassing as in (b).

samples were activated under N_2 (10^5 Pa, WHSV = 5 h^{-1}) at 673 K/14 h. In the case of toluene alkylation, a mixed feed (diluted with N_2) with a molar methanol/toluene ratio of ca. 1/4 (WHSV = 5 h^{-1}) was admitted to the catalyst and allowed to react at 673 K. Since toluene disproportionation exhibits lower reactivity than toluene alkylation over HZSM-5, a longer contact time (WHSV = 0.5 h^{-1}) with a higher temperature (753 K) was necessarily used for obtaining reasonable activity. The reaction products of both processes were analyzed by GC using a 5% SP-1200/1.75 Bentone-34 on Chrom WHP (100/120 mesh) column. The major reaction products could be analyzed at 343 K. Aromatics higher than C_9 were separated by the GC column at increasing temperatures programmed at 10 K min^{-1} to 393 K and proven not to be in significant amounts. Analyses at increasing time intervals were performed to study changes in both catalytic activity and selectivity with time.

RESULTS

The State of Boron

IR spectroscopy proved useful in identifying the state of impregnated boron. The IR spectra (Fig. 1) of the modified zeolite show new absorptions (not found for the parent zeolite) at ca. 3230, 2500, 2350, 2270, 1440, 1195, and 885 cm^{-1} (Fig. 1a, with the zeolite spectrum being subtracted and samples not calcined). The OH-associated bands, particularly the absorption at 3230 cm^{-1}, has disappeared from the spectrum of calcined samples (vacuum at 0.133 mPa/673 K/2 h.), see Fig. 1b. The former spectrum (Fig. 1a) is more typical of boric acid than boric oxide (*23*, *24*). The most important feature observed for calcined samples (Fig. 1b) is the appearance of new absorption (not found for either the parent zeolite, Fig. 1c, or boric acid, Fig. 1a) at ca. 930 cm^{-1}. It is similar to that observed for the borosilicate system and is characteristic of $=B-O-Si\equiv$ linkages (*25*, *26*). The formation of such a species on HZSM-5 reveals that a condensation reaction has occurred between boric acid and zeolite Brønsted sites during calcination. Indeed, spectral investigation in the OH stretching region reveals a decrease in the absorbance of the band associated with the zeolite Brønsted sites as boron content increases (Figs. 1b,c). Inves-

TABLE 1

Zeolite Treatment and Chemical Analysis

Catalyst	Treatment[a]	Atoms per unit cell			
		Si	Al	B	Na + K
HZSM$_0$-5	None	91.90	4.10	0.08	0.47
HZSM$_1$-5	Impregnated with H_3BO_3	91.90	4.10	1.58	0.47
HZSM$_2$-5	Impregnated with H_3BO_3	91.90	4.10	3.21	0.47
HZSM$_3$-5	Impregnated with H_3BO_3	91.90	4.10	8.53	0.47

[a] For the method of preparation, see example 7, Ref. (*16*).

tigation in the region of zeolite lattice vibrations (KBr disks) indicates that impregnation with boron has no effect on zeolite structure, since the 550/450 cm^{-1} band ratio characteristic of the ZSM-5 structure is not altered. X-Ray diffraction data support this with clear-cut evidence, since neither shifts in the peak positions even at high 2θ values nor changes in the relative intensity of the ZSM-5 pattern have been detected.

Using the strongest absorption of boric acid at ca. 1440 cm^{-1} (ν_{B-O}) (*24*), a comparison between boron content as estimated from the ir A_{1440} band absorbance and that of chemical analysis (Table 1) reveals, as would be expected, a linear dependence (Fig. 2b). However, a similar comparison between the Brønsted site (3610 cm^{-1}) band absorbance and boron content (Fig. 2a) reveals a linear dependence for the low boron content samples and deviation for the high boron content sample. This may indicate that while boron locates totally within the zeolite grain and neutralizes Brønsted sites for the low boron content samples, part of the boron does not neutralize remaining Brønsted sites for the high boron content sample, presumably because it locates on the external surface for that sample. Linear extrapolation to the minimum band absorbance of the 3610-cm^{-1} mode, corresponding to the high boron content sample (Fig. 2a), reveals that ca. 6 boron atoms per zeolite unit cell neutralize Brønsted sites. X-Ray photoelectron spectroscopy (XPS) provides some complementary data. A comparison between boron/silicon (B/Si) ratio as found in the bulk (chemical analysis) and on the surface (XPS) of the zeolite grain for HZSM$_1$-5 and HZSM$_3$-5 shows consistency for the former and inconsistency for the latter zeolites. B/Si ratios of

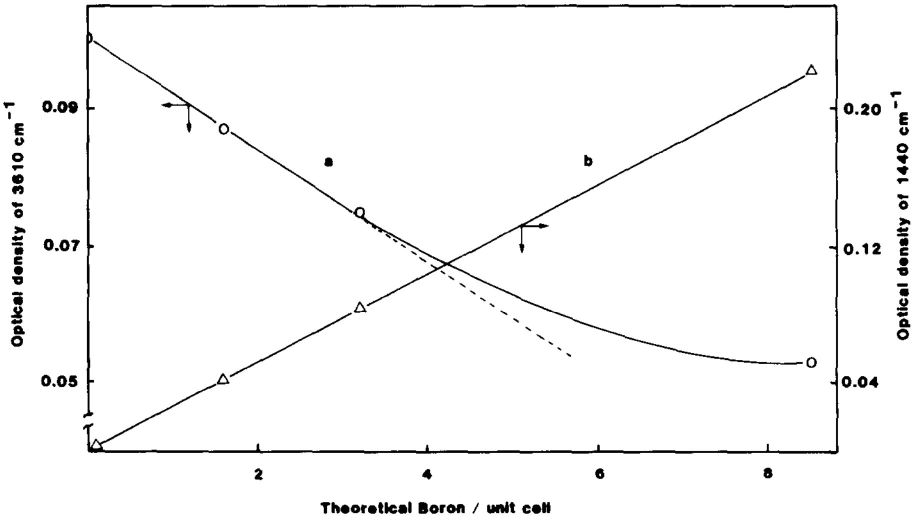


FIG. 2. (a) Dependence of the A_{3610} band intensity of the Brønsted sites on boron content. (b) Variation of the A_{1440} band intensity of boric acid vs chemical analysis for boron.

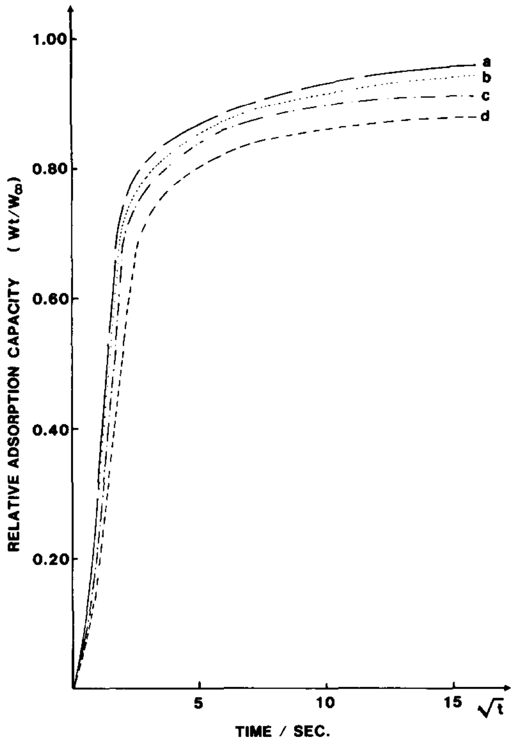


FIG. 3. The kinetics of 3-methylpentane sorption at 293 K and their variation with boron content. (a) HZSM$_0$-5, (b) HZSM$_1$-5, (c) HZSM$_2$-5, and (d) HZSM$_3$-5.

0.03 and 0.23 have been found for HZSM$_1$-5 and HZSM$_3$-5, respectively, by XPS versus 0.02 and 0.09, respectively, by chemical analysis. It may therefore be concluded that part of the boron for the high boron content sample, HZSM$_3$-5, locates at the external surface of its zeolitic grains.

It is also possible that because of the calcination of the boron-impregnated samples at 773 K in flowing air for 16 h some of the boron is incorporated into the zeolite framework at Si or/and Al locations. The MAS-NMR technique has proven to be an excellent technique to give information about such a possibility. Usually a very narrow line of ^{11}B is observed only in the case of lattice boron nuclei, whereas no peak or a broader peak with possibly side bands are detected for borosilicate glasses, for instance (*27, 28*). Moreover, a change in (Si/Al)$_{latt.}$ ratio as calculated from NMR (*29*) Si lines (Si-0Al and Si-1Al) could be detected. A MAS-NMR study on our all four samples was carried out at Namur by Professor J. B. Nagy. It was observed that actually boron atoms were incorporated in place of Si atoms into the lattice but their amount is rather small and cannot account for the physical and catalytic features observed in the present work.

Effect of Boron on Sorbate Diffusion and Capacity

Sorption of the hydrocarbons *n*-hexane and 3-methylpentane has been followed by thermogravimetry. Because of its lower diffusivity within ZSM-5, the sorption of 3-methylpentane was preferentially studied kinetically. Figure 3 shows the difference in sorption kinetics for 3-methylpentane/HZSM-5 as a function of boron content. Both sorption kinetics (Fig. 3) and sorption capacity (Table 2) decrease with boron content. Figure 4 shows the dependence of sorption capacity on equivalent boron content for 3-methylpentane/HZM-5. While it is linear for the low-boron samples, the high-boron sample, HZM$_3$-5, deviates. Linear extrapolation to the minimum sorption capacity, corresponding to HZM$_3$-5, reveals that an equivalent theoretical 5 boron atoms per zeolite unit cell are effective due to incorporation within the zeolite channels. The rest of the boron for this sample probably locates on the external surface, and does not affect the sorption capacity.

TABLE 2

Data From Hydrocarbon Adsorption

Catalyst	Adsorption capacity (wt%)		Equivalent theoretical boron atoms/unit cell	
	n-Hexane	3-Me pentane	Calculated[a]	Chem. anal.
HZSM$_0$-5	11.54	7.10	0.00	0.00
HZSM$_1$-5	11.25	6.50	1.63	1.58
HZSM$_2$-5	10.85	5.85	3.42	3.21
HZSM$_3$-5	9.96	5.17	5.26	8.53

[a] From pore void volume not occupied by 3-methylpentane.

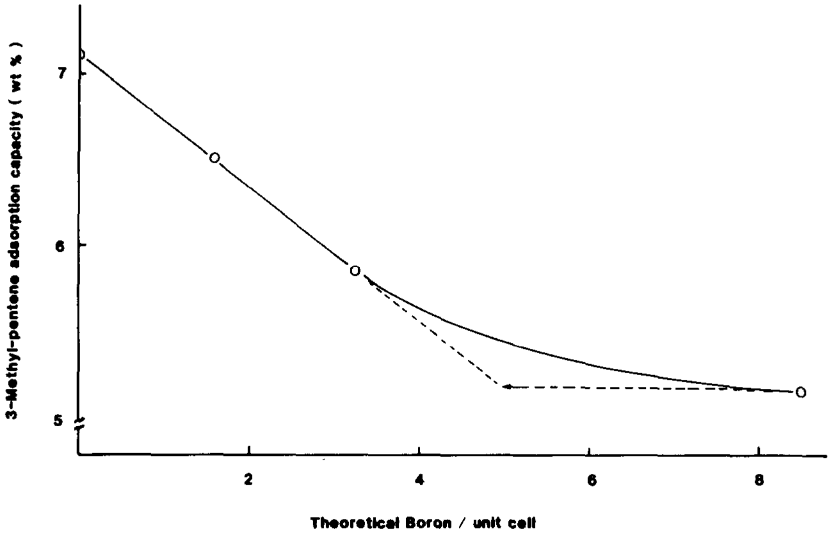


FIG. 4. The dependence of 3-methylpentane sorption capacity on boron content. Maximum sorption capacity was measured after prolonged sorption (~16 h) at a pressure of 400 Pa and 293 K.

Since 3-methylpentane adsorbs end to end and does not exhibit overlapping of molecules at the channel intersection (*29*), the loss in sorption capacity may be appropriately used for estimating the equivalent theoretical boron content within the channels, which is associated with sorption loss. Having given the molecular volume of both boric acid and 3-methylpentane, calculation based on the zeolite pore volume filled with the modifier reveals that the loss in 3-methylpentane correlates linearly with boron content (Table 2). While the results show consistency with those of chemical (bulk) analysis for $HZSM_I$-5 and $HZSM_2$-5, a lower value is revealed for $HZSM_3$-5. The inconsistent value, 5.26 (Table 2), corresponds very well with the value given by linear extrapolation, 5 (Fig. 4), which confirms linear dependence. These results, together with the spectral findings, indicate that ca. 5–6 equivalent theoretical boron atoms per zeolite unit cell are the maximum held within the zeolite grain, the remainder presumably lying on the external surface.

Boron Mobility

(*i*) *Toluene alkylation by methanol.* In order to minimize the activity of the catalyst for methanol self-conversion over HZSM-5, a mixed feed of methanol/toluene with molar ratio ca. 1/4 was used for toluene alkylation. A blank test showed that there was insignificant reactivity for such a self-conversion relative to the dominant alkylation process. As a result, ca. 25 mole% toluene conversion is the maximum (theoretical) activity for the present system. The activity of the different samples (Fig. 5) starts (5 min) with lower values reaching maxima (within 15–30 min), which may be slightly higher than the theoretical value. Higher activities may contribute to limited toluene disproportionation and/or dealkylation, which is indicated by fractions of benzene product. Although activity is maintained high for the parent, $HZSM_0$-5, it progressively decreases with boron content for the modified samples (Fig. 5). Except for anomalous behavior detected for $HZSM_I$-5, the decrease with time is almost linear. For $HZSM_I$-5, the activity starts at a high level, comparable with that for $HZSM_0$-5, then unexpectedly drops with time followed by a steep rise almost to the original high level in a way associated with the selectivity change (see later). The activity for this sample then follows normal

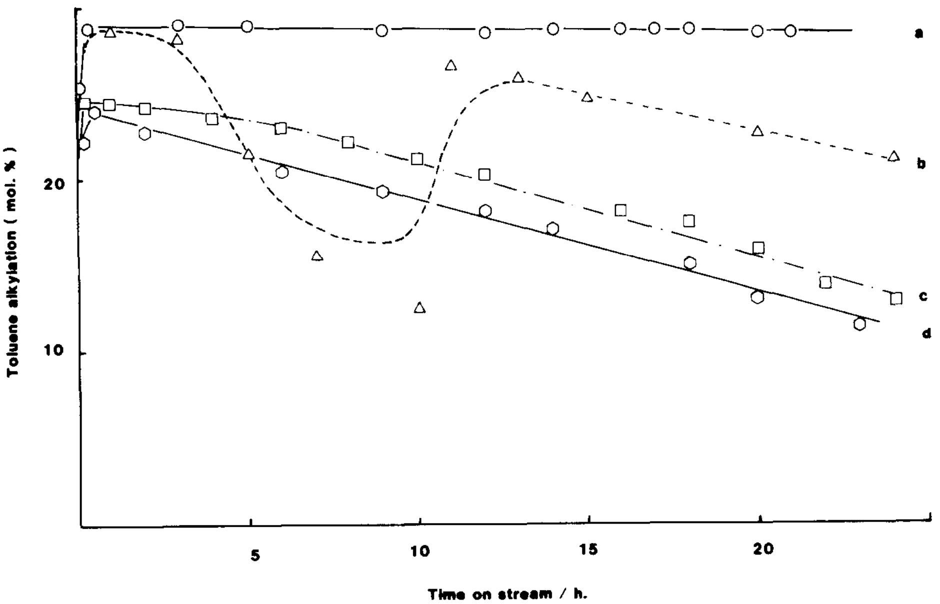


FIG. 5. Variation in toluene alkylation activity with time on stream. Reaction conditions: a feed of methanol/toluene molar ratio of 1/4 was passed with WHSV (5 h^{-1}) over ZSM-5 (50 mg) at 673 K. Notation as for Fig. 3.

behavior with time, with a linear dependence as shown for the other samples. This anomalous behavior was also observed for other samples of the same batch, but its amplitude and the time at which activity rose again were different, although similar. Moreover, if the samples were regenerated by oxygen treatment this behavior was not observed, rather as if a stabilization had occurred.

Consistent with the activity change described above, the selectivity (to *p*-xylene) also changes. Figure 6 shows the trends of selectivity change with time for the different samples. Both the parent, $HZSM_0$-5, and highly modified $HZSM_3$-5 samples show the two selectivity extremes. $HZSM_0$-5 shows the lowest selectivity (ca. 60%) and $HZSM_3$-5 shows the highest selectivity (ca. 90%). While the selectivity of both samples is maintained over 10 h of reaction, it thereafter drops regularly with time for $HZSM_3$-5 and only slightly for $HZSM_0$-5. The most dramatic change is observed for the lowest boron content sample, $HZSM_1$-5 (Fig. 6). Selectivity starts low as if the sample were not modified, then increases in a way associated with the activity drop (Fig. 5). At t = 10 h the selectivity (Fig. 6) reaches a maximum as activity (Fig. 5) reaches a minimum. The selectivity then decreases with time.

It is important to point out that at the end of the process (48 h), not shown in Fig. 6, the alkylation for all the modified samples exhibits almost similar selectivities to that of the parent zeolite, ca. 55%.

(*ii*) *Toluene disproportionation.* Since activity for toluene disproportionation is lower than for toluene alkylation, longer contact time and higher temperature were necessary to raise the activity of this system to levels comparable to alkylation. Changes in activity and selectivity for this system were studied in a similar manner as for alkylation. The changes in activity for the different samples are depicted in Fig. 7. In contrast to toluene alkylation over the parent zeolite, which exhibits high activity maintained for a long reaction time,

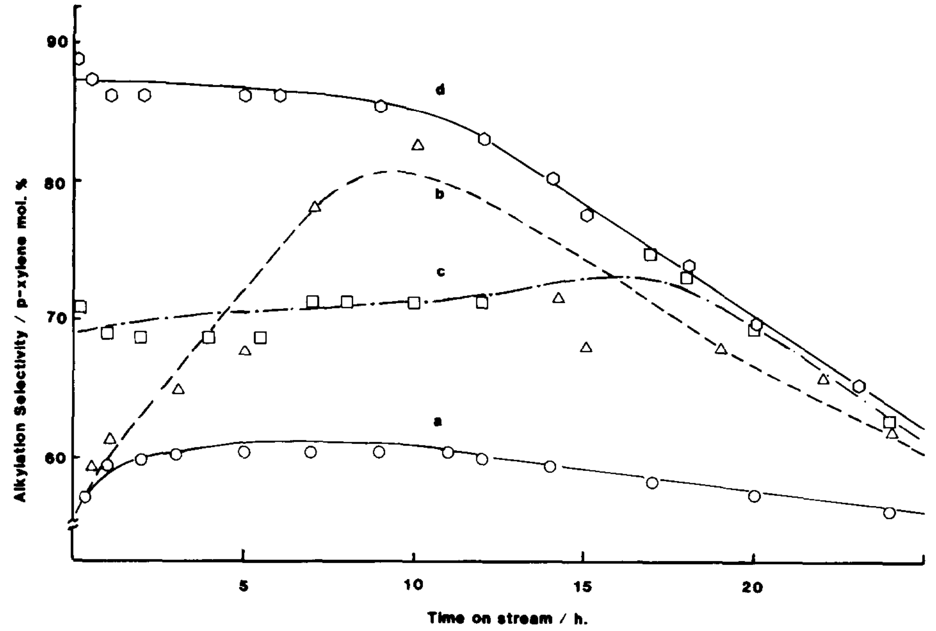


FIG. 6. Variation in toluene alkylation selectivity with time on stream. Reaction conditions and notation as for Fig. 3.

the disproportionation over the same sample exhibits an activity which falls with time, reaching a low level within a short period. However, the activity of the highly modified sample, HZSM$_3$-5, is low for 10 h of reaction time, then suddenly increases (Fig. 7), followed finally by a decrease with time. As for alkylation, toluene disproportionation over HZSM$_1$-5 exhibits activity varying with time in a complex trend. The

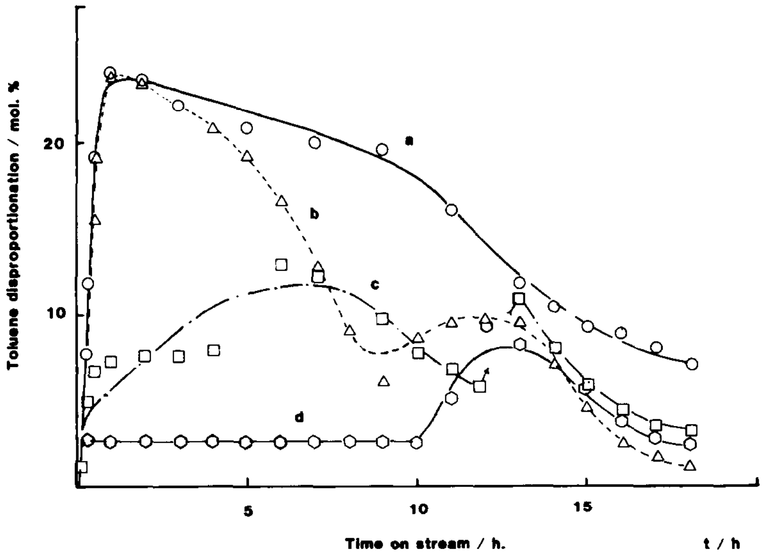


FIG. 7. Variation in toluene disproportionation activity with time on stream. Reaction conditions: a feed of toluene was passed with WHSV (0.5 h^{-1}) over ZSM-5 (50 mg) at 753 K. Notations as for Fig. 3.

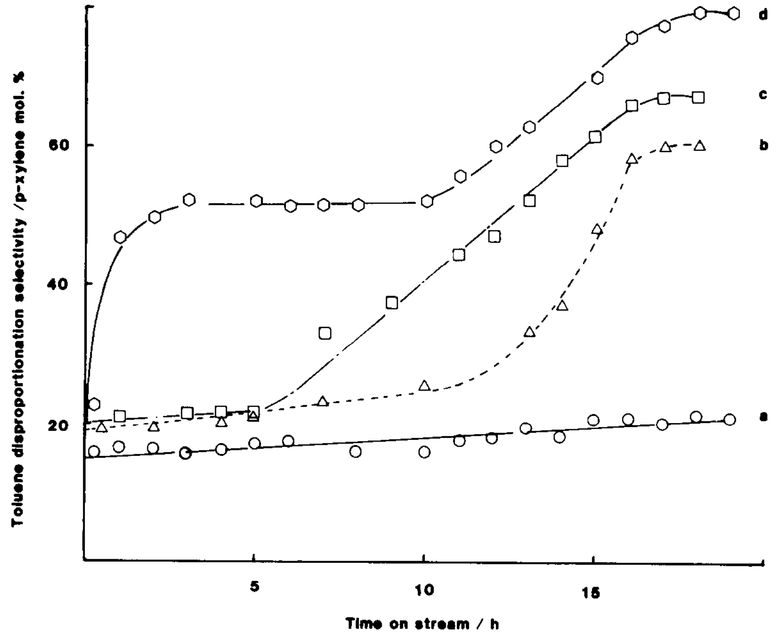


FIG. 8. Variation in toluene disproportionation selectivity with time on stream. Reaction conditions and notation as for Fig. 7.

reaction period around 10 h appears to be critical. The sample starts with an activity as if it is not modified, but suddenly the activity drops with time reaching a minimum at 10 h, then increases followed by further decrease. The activity of the moderately impregnated sample, $HZSM_2$-5, as expected, follows a moderate but rather unregular trend.

The change in selectivity for this system is also contradictory to alkylation. While selectivity in alkylation decreases with time (Fig. 6), it increases with time for disproportionation. The increase is more pronounced for the more boron-containing samples (Fig. 8). As expected, both the parent nonmodified and the highly modified samples show the two selectivity extremes. They show the lowest and highest selectivities, respectively. A minor change in selectivity with time is shown for $HZSM_0$-5, and a major rise with time for $HZSM_3$-5. Other moderately impregnated samples show moderate increases in selectivity with time.

Generally, while selectivity in alkylation gives predominantly *p*-xylene (ca. 60%), increasing with boron content (Fig. 6), it gives predominantly m-xylene (ca. 62%) in the disproportionation system, with *p*-xylene (ca. 18%) significantly increasing with boron content. Also, as for alkylation, while boron influences the distribution of xylene isomers, it does not affect the total amount of xylenes in the disproportionation products. It is also interesting to observe that, in contrast to toluene alkylation, the final xylene distribution shows selectivity maintained at high levels for the modified samples. Another uncommon trend observed for all samples in the present system is that the reaction starts by yielding predominantly benzene (ca. 90%), as toluene would be dealkylated, then gives, as expected, an equal mixture of benzene and xylenes, and surprisingly ends with a benzene/xylenes mixture of molar ratio ca. 1/2.

Higher aromatics form in more significant quantities for toluene alkylation than for its disproportionation. They are dominated by ethyltoluene and trimethyl benzene rich in the less bulky isomers. While the proportions of the former decrease with time, those of the latter increase. Moreover, ethylbenzene forms in lesser quantities for toluene alkylation than disproportionation.

A blank test of boric acid activity was carried out for both catalytic processes over silicalite (impregnated with ca. 1.6 boron/unit cell). The results reveal no activity except for minor amounts of dimethylether forming from methanol self-conversion.

The present investigation agrees with the findings of Kaeding *et al.* (*16–19*) in a more expanded form. A model to understand the role of the modifier is now needed to discuss the different trends observed for activity and selectivity changes in the present study with reference to the findings of Kaeding *et al.*

DISCUSSION

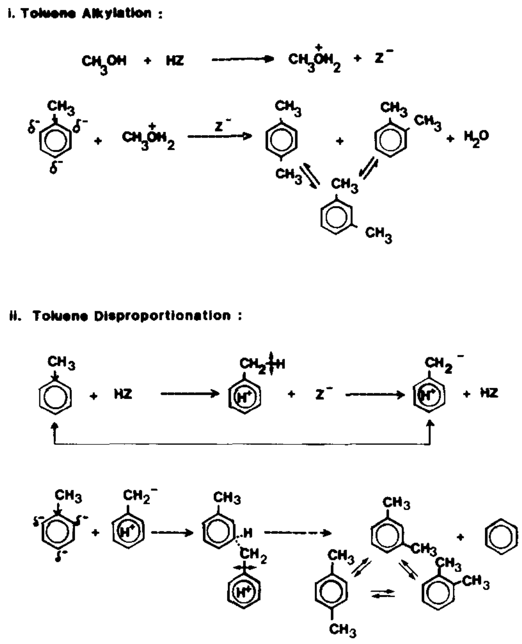
The key points in the study of Kaeding *et al.* (*16–19*) which have been the stimulus of this investigation can be summarized as follows:

—decreased in selectivity (to *p*-xylene) with time for toluene alkylation;
—increase in both selectivity and activity with time for toluene disproportionation;
—regeneration of the catalyst by calcination in air/H_2O gives an increase in activity, but a reduction of selectivity for the modified zeolite in toluene alkylation;
—detection of benzene in mole% exceeding the expected value, ca. 50%.

For providing a model capable of linking these unusual changes to the modifier, characterization of the modifier has been of essential importance. As shown by ir spectroscopy, boron is present in the form of boric anhydride linked to the zeolite framework as has been previously proposed for phosphorus (*30*). The borosilicate structure proposed for the present model should not be confused with a different borosilicate structure presented in other work (*31*). Boron in the latter case is fully embodied in the zeolite framework, taking the fixed position of aluminum, while boron in the present model occupies a mobile Brønsted site. Under steaming, boron reverts to mobile boric acid and the Brønsted site is relieved, as is evident in the IR spectra. For hydrated samples, the absorption at 930 cm^{-1} characteristic of $=B—O—Si\equiv$ structure disappears from the modified zeolite spectrum with the appearance of typical boric acid spectrum. General agreement between IR, TG, and XPS techniques shows complete accommodation of boron within the zeolite grain for the low boron content samples, $HZSM_1$-5 and $HZSM_2$-5, and only partial accommodation for the high boron content sample, $HZSM_3$-5. Moreover, it is revealed by these techniques and calculation that ca. 5–6 boron atoms per unit cell can be accommodated in the channels' within the zeolite grain.

Based on these findings, a model based on the state of boron and the reaction mechanism of the catalytic process can be suggested to explain the different trends observed for the activity and selectivity changes. It is clear that while boron regularly fills the channels of $HZSM_3$-5, a less regular filling occurs, more pronounced for the lesser boron content sample $HZSM_1$-5 than for $HZSM_2$-5. Of course the unfilled channels of the nonmodified sample $HZSM_0$-5 are regular. Therefore, based on the fact that selectivity is shaped according to the catalytic atmosphere, more regular channel pathways result in more regular behavior, and vice versa. The matter is more pronounced if mobility of the modifier is involved. This results in complex activity and selectivity changes, the more mobile the boron the more complex is the catalytic behavior.

For toluene alkylation, steaming occurs as a result of water formation (Scheme 1). This would mobilize boron within the zeolite grain. More boron mobility is expected for the less filled zeolite channels, and therefore more irregular catalytic behavior. This is clearly shown in Fig. 5. Irregularity



SCHEME 1.

increases in the order: HZSM$_0$-5 < HZSM$_3$-5 < HZSM$_2$-5 < HZSM$_1$-5. Since the reaction preferentially occurs at the channel intersections, competition would force relieved unreactive boric acid to move out into the narrower channels causing modified selectivity, then away to the external surface causing loss in modifed selectivity. This sequence is more pronounced for the more mobilized boron samples, e.g., HZSM$_1$-5 and HZSM$_2$-5. At the end of the alkylation, most of the modifier, boron, is cleared away, and therefore the original nonmodified selectivity is restored for all samples. This would explain why reinforcing the catalyst with a fresh portion of boron at the end of the process (*16*) is essential for regenerating modified selectivity.

If the above argument is correct, then other systems involving less of the steaming problems should yield more regular selectivity change. Indeed, this is shown for toluene disproportionation (Fig. 8). Selectivity for this system increases with time with more pronounced extents for the more boron content samples. Regular increase in shape selectivity for this system is most probably attributed to limited mechanical boron mobility. Since toluene disproportionation involves bulky biphenylmethane intermediate formation, the reaction essentially proceeds at the intersections. Therefore, clearing boron away the intersections is essential. Since water is not involved, this mechanical removal would take a long time, and therefore a complete boron removal out of the channel system is difficult. This would explain the stepwise increase in selectivity (Fig. 8) over long reaction time and the selectivity being maintained at a high level, corresponding with the zeolite boron content, at the end of the reaction for this system, which is at variance with that for the alkylation system discussed above.

The gaps separating the activity levels for toluene disproportionation (Fig. 7) are higher than those for alkylation (Fig. 5). This would support the argument that steaming for the latter assists in mobilizing, and therefore removing, boron out of the channel system. Thus, the gaps separating activity for the different samples under alkylation are diminished as a result of reducing the effect of the modifier within the zeolite grain. Catalyst deactivation with time is most probably a consequence of surface coking. Disproportionation activity drops with a higher order than for alkylation, which is consistent with the fact that much of the boron modifier is still accommodated within the zeolite grain, and therefore masks many of the active sites and reduces the diffusivity of both reactants and products.

The production of dominant *p*-xylene for alkylation and dominant *m*-xylene for disproportionation of toluene over the nonmodified sample is necessarily a matter of different mechanisms being involved (see Scheme 1). External surface activity of the zeolite cannot be invoked to explain different selectivities, since the present parent zeolite shows high selectivity to *p*-xylene (60%), which is maintained over a long range of reaction time. High external surface reactivity is known to assist xylene isomerization to nearly the thermodynamic equilibrium distribution (*21*).

Reaction Mechanism

(*i*) *Toluene alkylation.* Because of the inductive effect of CH_3 within the benzene ring, the basicity of the ring is concentrated on the *o*- and *p*-positions. Therefore, electrophilic $CH_3\overset{+}{O}H_2$ would preferentially attack those positions, yielding dominant *o*- and *p*-xylenes and less *m*-xylene. This would change under the influence of shape-selectivity catalysis. For ZSM-5, the zeolite structure would favor the formation of *p*- to *o*-xylenes in the primary reaction products.

Moreover, because of increased diffusion limitation a higher yield of the less bulky isomer (*p*-xylene) is expected. Such a limitation may be introduced by an inorganic filler within the channels as for P (*30*) and presently for B or by increased particle size (*21*, *32*).

(*ii*) *Toluene disproportionation.* The dominance of *m*-xylene in the reaction products and the mechanism involved for this system need an appropriate explanation that has not yet been provided. The dominance of *m*-xylene for this system has been recognized whether the catalytic process is homogeneous or heterogeneous. Moreover, this has been observed even for the shape-selective zeolite, ZSM-5, whether the particle is small or large, unless the zeolite is otherwise modified by impregnation. Olson and Haag (*21*) have commented on this matter concluding that the primary xylene products form with *o*- and *p*-xylenes being the dominant isomers, which is followed by isomerization to the thermodynamic equilibrium as a result of reaction proceeding at low WHSV.

In fact the model selected by Olson and Haag (*21*) (toluene alkylation by benzyl chlorides) cannot be appropriately used to describe toluene disproportionation, since different mechanisms are involved. In toluene alkylation by benzyl chloride, the attacking species, $Ph.CH_2^+$, is of electrophilic nature, and therefore, is directed to the more basic *o*- and *p*-positions of the toluene ring. In contrast, for toluene disproportionation, the attacking species, $Ph.CH_2^-$, is of nucleophilic nature, and therefore is directed to the less basic *m*-position of the toluene ring (Scheme 1). Thus, reaction products dominated by *m*-xylene for the present system is a mechanistically dependent process, and is not the result of isomerization, particularly if the sample does not exhibit external surface reactivity as for the present case.

Finally, the uncommon sequence of reaction for disproportionation of toluene which starts by yielding dominant benzene and ends by yielding dominant xylene can be interpreted in terms of reaction proceeding in sequence as follows. At the start, channel intersections are occupied by boron, and therefore toluene is forced to react within the narrower channels, which does not accommodate its disproportionation, and hence the reaction is altered to dealkylation yielding predominantly benzene. Following this, toluene distribution within the grain, particularly at the intersection, is improved with time as a result of boron displacement, and therefore disproportionation of toluene becomes possible and, as expected, an equal benzene/xylenes mixture is obtained. Finally, some of the trapped methyl groups resulting from the previous step (light aliphatics are not detected) would disturb the equilibrated mixture with another source of alkylation, which gives rise to more xylenes than would be expected.

CONCLUSIONS

Different reaction pathways favor the formation of *p*-xylene for alkylation and *m*-xylene for disproportionation of toluene. ZSM-5 modification with boron, as shown in the present study, proves useful in enhancing the formation of *p*-xylene in both catalytic processes. However, boron mobility within the zeolite grain reduces the modified selectivity with time on stream, which reduces the usefulness of such modification processes on the industrial scale. The present data show that selecting the modifier with regard to the catalytic process is of essential importance. The modifier should be selected as to be stable and not to be affected by the catalytic process under the experimental conditions.

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