*Characterization of the Alumina-Boria Catalyst**

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Alumina-boria is a well-known type of acidic cracking catalyst.(1,2) However, the details of its characterization still remain unsettled, in contrast to the case of silica-alumina, which has been the subject of numerous investigations. It has been previously suggested(3-6) that active alumina may react with boric acid to form strongly acidic centers, but more experimental evidence is necessary for an understanding of the reaction and of a probable mechanism of the development of activity. Although Ikebe(4) showed the remarkable effect of the chemical composition of alumina-boria upon its cracking activity, little is known so far about the best method of preparing the catalyst. This study was undertaken in order to obtain such information.

The present investigation started from the observation that the activity of alumina-boria was considerably affected by the chemical and the physical nature of the alumina used as the catalyst-base, the effect of the conditions of catalyst preparation upon the activity of the toluene disproportionation was examined. In the second step, the chemical interaction of active alumina with boric acid was studied by thermographic analysis, and the mechanism of developement of activity was discussed on the basis of the results, together with those of X-ray diffraction, infrared absorption and the colorination of adsorbed indicators. Kinetic studies of some specific reactions over alumina-boria were made in order to establish the applicability of the catalyst.(7-11)

Experimental

Alumina as a Catalyst Base.—A hydrous alumina gel was prepared at a given pH by adding an aqueous solution of ammonia (4 N) to a solution of aluminum nitrate (10%). The precipitate was washed to remove nitrate ion and dried in an electric oven for several hours at 130°C to form an alumina hydrate. The greater part of the alumina

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* This paper is an abridgment of a series of studies of the alumina-boria catalyst previously published.(7-11)

1) W. A. Bailey, U. S. Pat 2377744 (1945.)

2) N. V. de B. P. M., Dutch, Pat. 65287 and 62287.

3) C. L. Thomas, *End. Ing. Chem.*, **41**, 2564 (1949).

4) K. Ikebe, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **61**, 437 (1958).

5) K. Ikebe, ibid., **61**, 575 (1958).

6) K. Ikebe, N. Hara, K. Mita and K. Shimizu, *J. Fuel Soc. Japan* (*Nenryo Kyokai Shi*), **37**, 257 (1958).

7) Y. Izumi and T. Shiba, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **84**, 699 (1963).

8) Y. Izumi and T. Shiba, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zasshi*), **66**, 1817 (1963).

9) Y. Izumi and T. Shiba, ibid., **67**, 559 (1964).

10) Y. Izumi and T. Shiba, ibid., **67**, 564 (1964).

11) Y. Izumi N. Idemoto and T. Shiba, Catalysis Club of Japan, *Shokubai* (*Catalyst*), **5**, 277 (1963).

hydrate, which was obtained at pH 10 with or without the aging of the precipitate, was found to consist of bayerite, while the alumina hydrate prepared at pH 7 to 8.2 showed a clear diffraction pattern assigned to gibbsite. It was suggested that the particle sizes of these two kinds of aluminum trihydroxide might be supposed to be very fine,[12,13] since only one endothermic peak was observed, at about 330 to 370°C, in the course of the thermal transformation.[7] Gibbsite and bayerite were dehydrated by calcination at 300 to 600°C in a muffle furnace for several hours, and transformed into χ-alumina and η-alumina respectively, as is shown in Table I.

TABLE I. X-RAY ANALYSIS OF ALUMINA FOR A CATALYST BASE

Condition of precipitation pH, aging	Calcination temp. °C	Structure of alumina	Relative intensity of maximum diffraction peak*
10, none	130	Bayerite Gibbsite	>100 20
	300	η-Alumina	7
	400	η-Alumina	10
	500	η-Alumina	15
	600	η-Alumina	18
10, 30 days	130	Bayerite Gibbsite	>100 20
	300	η-Alumina	8
	400	η-Alumina	10
	600	η-Alumina	20
8.2, 30 days	130	Gibbsite	>100
8.0, none	400	χ-Alumina	7
8.0, 30 days	400	χ-Alumina	8
7.0, none	400	χ-Alumina	3
7.0, 30 days	400	χ-Alumina	7

* Angular position of the maximum diffraction peak (2θ); gibbsite 18.3°, bayerite 18.8°, η-alumina 66.8°, χ-alumina 67.2°.

The Preparation of Alumina-Boria.—Both hydrous and anhydrous alumina were used as catalyst bases. Powdered alumina was impregnated with the required amount of an aqueous solution of boric acid, and the mixture was heated in a kneader by an infrared lamp in order to evaporate the excess water. The resulting wet composite was pelleted into cylindrical form (4 mm.$\phi \times$4 mm.); then the pellets were calcined at 400 to 500°C for 4 hr. in a muffle furnace.

The Determination of Boria Content.—Boron in silicate ores is generally determined by a fusion method, but in the present case it was found that boric acid was so easily extracted from the catalyst with hot water that an almost complete determination was possible by means of titration with a sodium hydroxide solution in the presence of mannitol. The boria content thus determined agreed well with that determined by the fusion method,[14] as well as with that calculated from the amount of boric acid which was impregnated into the alumina. Such easy extraction of boric acid suggests that the structure of alumina-boria may be very different from that of aluminum borate. All the boria contents shown in the experimental results were calculated from the amount of boric acid used in the catalyst preparation (B_2O_3/cat., wt.%).

Reaction Apparatus and Product Analysis.—Some specific reactions over an alumina-boria catalyst were carried out with a fixed-bed flow reactor under atmospheric pressure. The reactor consisted of a Pyrex double tube (24 mm.$\phi \times$600 mm.—10 mm.$\phi \times$ 600 mm.) and a feeder which was a syringe driven by a clock sinker. The reactor was placed vertically in a fluidized bed of powdered alumina with automatic temperature regulation.

The reaction products were analyzed by gas chromatography at 80°C using a column packed with 30% D. O. P. on celite. For the separation of xylene isomers, a 5 m. column of 30% 7,8-benzoquinoline[15] was used.

Acidity and Acid Strength Measurements.—The acidity of alumina-boria was determined following Benesi's[16] and Leftin-Hall's[17] methods as modified by Shiba and his co-workers.[18] The total acidity was determined by *n*-butylamine titration, using benzeneazodiphenylamine as an indicator, and the Lewis acidity, by the chemisorption of triphenylmethyl chloride on alumina-boria. The difference between the total and the Lewis acidity was attributed to the Brönsted acidity.

Color tests were made[16] by transferring roughly 0.1 g. of a dried, powdered sample into a test tube which contained 5 ml. of dry cyclohexane, adding a few drops of a solution of indicator in cyclohexane, and, after leaving it overnight, observing the color of the adsorbed indicator. The indicators used were benzeneazodiphenylamine, dicinnamalacetone and benzalacetophenone. Their acidic colors are purple, red and yellow, and the values of $\mathrm{p}K_a$ are $+1.5$, -3.0 and -5.6 respectively.

Other Measurements. — The differential thermal analysis for the examination of chemical interaction between alumina and boric acid was carried out under atmospheric pressure. The sample holder was a quartz vessel 5 mm. in diameter and 20 mm. deep.

X-Ray diffractions were recorded by a Phillips X-ray diffractometer with Ni-filtered Cu-K_α radiation.

Infrared absorption measurement was made on samples in potassium bromide discs in the region between 2 and 16 microns, using a Shimadzu AR-275 spectrophotometer.

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[13] K. Sakamoto, *J. Ceram. Assoc. Japan* (*Yogyo Kyokai Shi*), **67**, C 114 (1959).

[14] K. Kimura, "Muki Teiryo Bunseki" (Inorganic Quantitative Analysis), Kyoritsu Shuppan, Tokyo (1954), p. 345.

[15] D. H. Desty, A. Goldup and W. T. Swanton, *Nature*, **183**, 107 (1959).

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[17] H. P. Leftin and W. K. Hall, Proc. Intern. Congr. on Catalysis, 2nd., Paris, No. 65 (1960).

[18] T. Shiba, M. Sato, H. Nishimura, A. Hattori and K. Yoshida, 16th Annual Meeting of the Chemical Society of Japan, Tokyo, 1963.

The Structural Effect of Alumina Used for a Catalyst Base

The relationship of the structure of alumina used for a catalyst base with both the activity and the acidity of alumina-boria is shown in Figs. 1 and 2. The conversion of toluene* is taken for the activity since the selectivity of the disproportionation of toluene is almost identical with the different catalyst compositions (the mole ratio of produced xylene to benzene was 0.9±0.05). Both the η-alumina and χ-alumina used for catalyst bases were calcined at 400°C so as to give maximum activities of the catalysts.

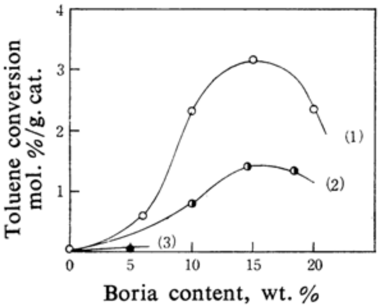

Fig. 1. Activity of toluene disproportionation over alumina-boria at 480°C.
Catalyst; 5.0 g. Feed rate: 0.030 mol./hr.
(1) η-Alumina base (2) χ-Alumina base
(3) α-Alumina base

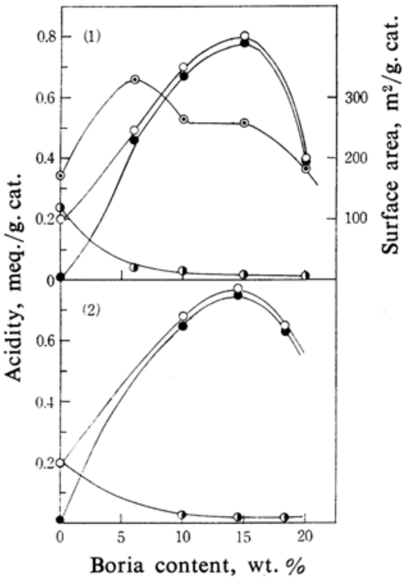

Fig. 2. Acidity of alumina-boria prepared from η-alumina (1) and χ-alumina (2).
○ Total acidity ◑ Lewis acidity
● Brönsted acidity ⊙ Surface area

The catalyst prepared from η-alumina gave a higher activity than that from χ-alumina, while α-alumina was an ineffective base. The maximum activity was obtained at 15 wt.% of boria** in both of the active catalysts. It is suggested that the excessive boria might have been deposited on active sites, so lowering the activity, since boria by itself showed little activity. The aging treatment of the alumina used for a catalyst base was found to have little effect on the activity.⁷⁾

The greater part of the acidic centers of alumina-boria are of the Brönsted type, as is shown in Fig. 2. By comparing Fig. 1 with Fig. 2, it may also be seen that the catalytic activity has a correlation with the Brönsted acidity. This information fits in well with the reliable conception that the reaction may proceed via a carbonium ion mechanism. The surface area of the catalyst did not have any definite relationship with the activity. The activity per unit of Brönsted acidity of the catalyst derived from η-alumina was much higher than of that derived from χ-alumina.⁷⁾ This may be due to the difference in acid strength or in the distribution of acid sites among the effective catalyst surfaces, because the structural deviation of η-alumina from χ-alumina is generally recognized as the difference in the distribution of aluminum ions among oxygen ions.¹²⁾

As for the synthetic silica-alumina, the catalyst of 50 wt. % of silica showed a best activity of toluene conversion (1.6 mol. %/g. cat. at the

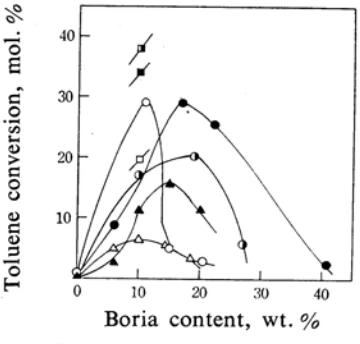

Fig. 3. Effect of the calcination temperature of η-alumina for a catalyst base upon the activity of toluene disproportionation at 480°C.
Calcined at 300°C ■, 400°C ◨, 500°C ○, and 600°C □. Dried at 130°C ◑ (bayerite).
Hydrous gel ●.
Catalyst: 20.1 g., feed rate: 0.0285 mol./hr.
Calcined at 400°C ▲, and 550°C △.
Catalyst: 5.0 g., feed rate: 0.0300 mol./hr.

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* The conversion represents the value which was obtained with an "equilibrated" catalyst. The decrease in activity with the length of run will be discussed later.

** Ikebe⁴⁾ has shown that the maximum cracking activity of alumina-boria is obtained at about 12~15 wt.% boria, and that the alumina used for his catalyst base contains hydrous alumina.

same condition as shown in Fig. 1) and the maximum Brönsted acidity (0.164 meq./g. cat.); the total acidity was 0.300 meq./g. cat. The result indicates that the activity per unit mass of the silica-alumina is much lower than that of the alumina-boria prepared from η-alumina. This is probably due to the lower concentration of acid sites in the former in spite of its higher activity per unit of Brönsted acidity.

The effect of the calcination temperature of the alumina used for the catalyst base upon the activity is shown in Fig. 3. The maximum activity was given by the catalyst which was derived from η-alumina calcined at 400°C. In view of the higher crystallinity of the alumina with the higher calcination temperature, it may be concluded that an alumina calcined at a higher temperature may be less reactive upon boric acid, resulting in a less effective base for the catalyst.

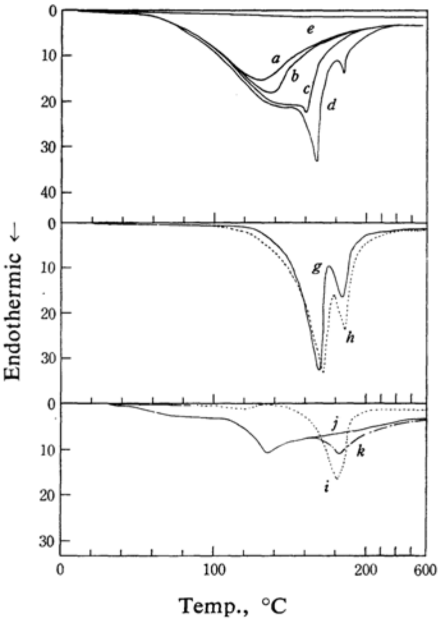

Fig. 4. Differential thermal analysis of the systems of alumina-boric acid (*a*, *b*, *c*, *d*, *g*) and alumina-metaboric acid (*i*, *j*, *k*).
Rate of heating: 4.4°C/min.
Standard side: η-alumina (0.1385 g.) for *a*, *b*, *c*, *d*, *e*, *j* and *k*. α-alumina (0.1385 g.) for *g*, *h* and *i*.
Sample side: η-alumina (0.1385 g.) with boric acid corresponding to boria content (%), *a* 15, *b* 20, *c* 25, *d* 30 and *e* 0. η-Alumina (0.1385 g.) with metaboric acid corresponding to boria content (%), *j* 15, *k* 30. α-Alumina (0.1385 g.) with boric acid corresponding to boria content (%), *g* 15. α-Alumina (0.1385 g.) with metaboric acid corresponding to boria content (%), *i* 30. *h* consists of boric acid alone (the same weight of boric acid as in the *a* sample).

The Development of Active Centers

The Chemical Interaction of Alumina with Boric Acid. — Ikebe and his co-workers[6] have shown that the thermogram of a hydrous alumina alone and that of an alumina impregnated with boric acid were almost identical. This result may be explained as an overlapping of the endothermic transformation of the hydrous alumina with the thermographic behavior of chemical interaction between alumina and boric acid. They concluded from an X-ray study that boric acid reacts with alumina at about 300 to 400°C on the basis of their observation of the disappearance of some sharp diffraction peaks of a mixture of hydrous alumina and boric acid at that temperature. However, a careful examination of their data shows that the interaction might have occurred at a lower temperature, since some angular locations of the diffraction peaks of the hydrous alumina* are almost identical with those of boric acid or of boron oxide.**

In the procedure of the differential thermal analysis in the present study, the probable thermal effects of alumina and the remaining water were eliminated, in order to obtain clear information about the interaction, by the use of a powdered anhydrous η-alumina as the reference and a dry mixture of the same weight of the alumina and various amounts of powdered boric acid as the sample. It is not unsuitable to test the chemical interaction by the use of the dry mixture because the activity of alumina-boria prepared from the dry mixture was almost identical with that of the catalyst derived by impregnation in an aqueous solution so long as the boria content was the same. The results of the differential thermal analysis are shown in Fig. 4. In the case of the η-alumina-boric acid system, the *a* or *b* composite (corresponding to 15 or 20% boria) gives only one broad endothermic peak, at about 130°C. On the other hand, the thermogram of the *c* or *d* composite (corresponding to 25 or 30% boria respectively) shows two sharp peaks, at approximately 170 and 185°C, besides a broad shoulder at 130°C. These peaks apparently accord with the two sharp peaks given in the transformation of boric acid alone (curve *h*) or of the α-alumina-boric acid system (curve *g*). Since two peaks of the *g* or *h* curve give no shoulder at 130°C, they clearly and even quantitatively correspond to

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* $2\theta=28.1°$ and 14.4° for boehmite with a strong intensity.

** $2\theta=27.9°$ (for H_3BO_3 and B_2O_3), and 14.6° for B_2O_3 with a medium intensity.

the transformations of boric acid into metaboric acid, and of metaboric acid into boria, respectively.[19] As for the η-alumina-metaboric acid system, a peak at 183°C in the thermogram of the *k* composite (corresponding to 30% boria), as well as a peak at 181°C of the *i* curve (metaboric acid), indicates the formation of isolated boria from metaboric acid, while the *j* composite (corresponding to 15% boria) gives only one endothermic peak, at 135°C. Judging from the results, it is probable that boric acid is dehydrated to form metaboric acid as an intermediate and that it reacts with an active anhydrous alumina at about 130°C to yield active centers, while boric acid does not react with α-alumina. It is also shown that excessive boric acid is transformed into isolated boria which might be deposited on the active centers and so lower the activity. The reactivity of χ-alumina with boric acid was found to be almost identical to that of η-alumina.[7]

The X-Ray Study of Alumina-Boria.—Table II gives the results of the X-ray diffraction of some catalysts with different compositions prepared from various forms of alumina. The relative diffraction intensity of the η-alumina which remains in the catalyst derived from anhydrous alumina is not very much reduced with the increase in boria content, whereas the intensity of the alumina in the catalyst made from hydrous alumina were remarkably reduced. This fact indicates that the reaction between anhydrous alumina and boric acid is probably localized on the surface of the alumina and that the crystal structure of alumina is not very much disturbed, whereas boric acid reacts more uniformly with hydrous alumina. In comparison with Fig. 3, it is supposed that excessive boria reduces the activity of alumina-boria because of the deposition of isolated boria. It is also shown that the reactivity of α-alumina with boric acid is very poor, since the diffraction of isolated boria appeared even in the composite of 5% boria. Attention must also be paid to the fact that alumina-boria did not give any definite diffraction pattern characteristic of aluminum borates such as $9Al_2O_3\cdot B_2O_3$, $2Al_2O_3\cdot B_2O_3$ and $Al_2O_3\cdot B_2O_3$.

TABLE II. X-RAY ANALYSIS OF THE ALUMINA-BORIA CATALYST CALCINED AT 500°C

Alumina for catalyst base	Boria content*	Structure of catalyst	Relative intensity of maximum diffraction peak**
Alumina gel without aging	0.0	η-Alumina	15
	6.2	η-Alumina	12
	16.8	η-Alumina	6
	21.9	η-Alumina	5
		Boria	4
	40.7	η-Alumina	5
		Boria	15
Bayerite	10.2	η-Alumina	11
	19.0	η-Alumina	4
		Boria	2
	27.1	η-Alumina	4
		Boria	4
η-Alumina	11.2	η-Alumina	14
	14.9	η-Alumina	12
	20.3	η-Alumina	12
		Boria	6
α-Alumina	5.0	α-Alumina	>100
		Boria	3
	15.0	α-Alumina	>100
		Boria	5

* Boria content (B_2O_3/cat., wt.%) represents the value determined by an extraction analysis except with the catalyst derived from α-alumina.

** Angular position of the maximum diffraction peak (2θ); η-alumina 66.8°, α-alumina 43.3°, boria 27.9°.

The Infrared Spectra of Alumina-Boria.—Among the spectra shown in Fig. 5, the spectrum of boria is quoted from Brame's publication.[20] The strong intensity band at 7 μ in the spectra of boric acid and boria is

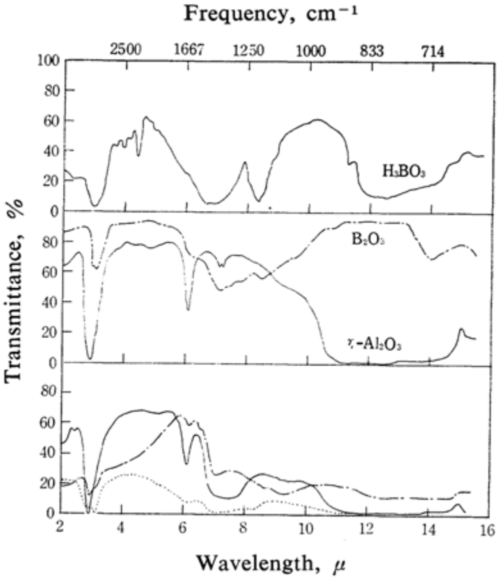

Fig. 5. Infrared spectra of boric acid, boria and alumina-boria.
——— : η-Alumina-boria (10% boria)
------ : η-Alumina-boria (30% boria)
—·—· : α-Alumina-boria (10% boria)

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19) J. Haladjian and G. Carpéni, *Bull. soc. chim. France*, [9], **1956**, 1679.

20) E. G. Brame, Jr., J. L. Margrave and V. W. Moloche, *J. Inorg. & Nuclear Chem.*, **5**, 48 (1957).

Table III. Coloration of Hammett indicators on catalysts

Sample	Calcination temp. °C	Hammett indicators (pK_a)		
		Benzeneazodiphenylamine (+1.5)	Dicinnamalacetone (−3.0)	Benzalacetophenone (−5.6)
η or χ-alumina alone	400	No change	—*	—
η or χ-alumina-boric acid (corresponding to 15 wt. % boria)	Without heating	Red	No change	—
	100∼200	Purple	Orange	No change
	300∼400	Purple	Orange	Yellow
Boric acid	Without heating	No change	—	—
Metaboric acid	100	No change	—	—
Evacuated boria	450	No change	—	—

* — Denotes that no further examinations were required.

assigned to the B–O vibration.[21-23] A slight shift in the position of the B–O vibration-band center towards longer wavelengths, as well as a considerable change in the band shape, was observed in the spectrum of the alumina-boria catalyst with 10% boria. In view of the mass effect[20] of the aluminum atom upon the B–O vibration, it is suggested that alumina may react with boric acid and that a B–O–Al bond is formed in the catalyst. On the other hand, the band position of the B–O vibration of the catalyst prepared from α-alumina (10% boria) accorded with that of boria. This shows that α-alumina is inactive for the interaction with boric acid. The disappearance of the B–O–H bending band in the case of the catalyst (10% boria) which appears at 8.3 μ with strong intensity in the spectrum of boric acid may suggest that such a bond as Al–O–B–O–Al is formed in the course of the fore-treatment of the catalyst.

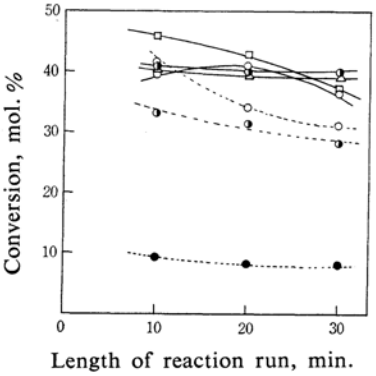

Fig. 6. Effect of the calcination temperature of catalysts upon activity.
Catalyst: η-Alumina-boria (10 wt. % boria) calcined at 300°C ●, 400°C ◑, 500°C ○, 600°C △, 700°C □.
——: Toluene disproportionation at 480°C, catalyst 20.1 g., feed rate 0.0285 mol./hr.
----: *o*-Xylene isomerization at 300°C, catalyst 6.0 g., feed rate 0.0520 mol./hr.

The Effect of the Calcination Temperature of the Catalyst upon the Activity.—The activities and acid strengths of some alumina-boria catalysts calcined at different temperatures are shown in Fig. 6 and Table III. It was observed that the heating of the mixture of active alumina and boric acid at a temperature as low as 100°C brought about an acid color with benzeneazodiphenylamine (pK_a +1.5), while the alumina alone and evacuated boria did not give the acid color by calcination, even at 400°C. This is consistent with the conclusion of the thermographic analysis. The data in Fig. 6, however, indicate that an effective catalyst for toluene disproportionation or for xylene isomerization could be obtained by calcination above 400°C. Since the catalyst gave an acid color with benzalacetophenone (pK_a −5.6) only when it was heated above 300°C, it may be concluded that the catalyst should be activated at a higher temperature than 400°C in order to develop the activity for these reactions. This is analogous to the finding of Topchiev's study of the alumina-chromia catalyst.[23] It is suggested, consequently, that the large amount of water which is produced in the course of chemical interaction between alumina and boric acid, and which still remains adsorbed on the resulting catalyst, hinders the development of activity.

Kinetic Studies of Some Specific Reactions over an Alumina-Boria Catalyst

The Disproportionation of Toluene.—A number of kinetic studies of the transalkylation

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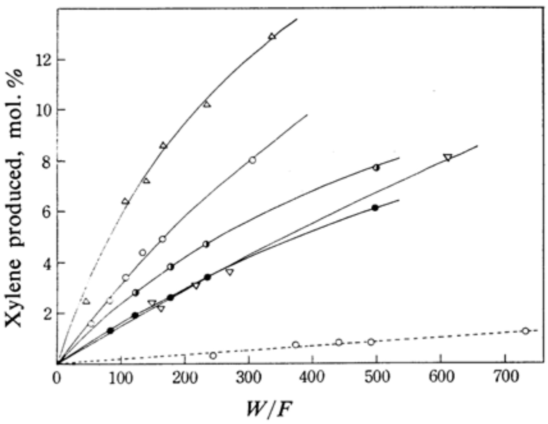

Fig. 7. Formation of xylene in toluene disproportionation
Reaction temperature (°C): 510 △, 480 ○◑ ●, 450 ▽.
Partial pressure (atm.): 1.0 △○▽, 0.8 ◑, 0.6 ●.
——: Fresh alumina-boria catalyst (10 wt.% boria, η-alumina for base). Stationary-state activity was almost identical with fresh and four times regenerated catalysts.
----: Commercial silica-alumina catalyst which was regenerated five times in order to obtain constant activity.

of aromatic compounds with solid acidic catalysts have been made by several workers.[24-28] However, few studies of these reactions with an alumina-boria catalyst have been kinetically forwarded. In the present paper, the role of the catalyst and the reaction kinetics are discussed. The results of the disproportionation of toluene at 450 to 510°C, with or without the dilution of the reactants with nitrogen, are shown in Fig. 7. Among the products, the quantity of benzene was larger than that of xylene in every run, and some cracking reactions (the demethylation of toluene and xylene) were found to occur simultaneously. A small amount of a gaseous substance was produced; it consisted of hydrogen and methane (in a 9 : 1 mol. ratio). These side reactions caused a decrease in the activity of the catalyst as a result of the coke formation. For this reason, the samples were taken when the activity became constant about an hour after the start of the run. The reaction scheme is expressed as follows:

Disproportionation:

$$2C_6H_5CH_3 = C_6H_6 + C_6H_4(CH_3)_2$$

$$\text{Cracking:} \left\{ \begin{array}{l} C_6H_5CH_3 \rightarrow C_6H_6 + CH_2\cdot \\ C_6H_4(CH_3)_2 \rightarrow C_6H_5CH_3 + CH_2\cdot \end{array} \right.$$

Johnson and Watson[24] studied the formation of toluene from benzene and xylene over a silica-alumina catalyst and showed that the rate was controlled by the surface reaction between the adjacent centers occupied by adsorbed reactants. In the present study, the disproportionation of toluene was likewise well interpreted kinetically by assuming that the rate was controlled by the surface reaction. The rate is described by an expression following the Langmuir-Hinshelwood mechanism;

Rate of disproportionation:

$$r_d = \frac{C_d(p^2_t - p_b p_x/K_d)}{(1 + K_b p_b + K_t p_t + K_x p_x)^2} \tag{1}$$

where C_d is the rate constant; K_d, the equilibrium constant of the disproportionation and p_b, p_t and p_x and K_b, K_t and K_x, partial pressures (atm.) and adsorption equilibrium constants for benzene, toluene and xylene respectively. Other expressions for the rate derived from the Rideal mechanism and the adsorption or desorption-controlling mechanisms were found to be unsuccessful in explaining the results of an examination of the relationship between the initial rate of the formation of xylene and the partial pressure of the feed. The overall rate of the reaction is given by the following expression, by assuming that the retardation term of the denominator of Eq. 1 is constant so long as the partial pressure of the feed is fixed;

$$\left. \begin{array}{l} \text{The rate of the formation of xylene:} \\ \quad r_x = dx/d(W/F) = k_d(p^2_t - p_b p_x/K_d)/2 \\ \qquad - k_x p_x \\ \text{The rate of the formation of benzene:} \\ \quad r_b = db/d(W/F) = k_d(p^2_t - p_b p_x/K_d)/2 \\ \qquad + k_t p_t \\ \text{The rate of subsequent cracking:} \\ \quad r_c = r_b - r_x \end{array} \right\} \tag{2}$$

where k_d, k_x and k_t denote rate constants of toluene disproportionation, xylene cracking and toluene cracking at a constant partial pressure of the feed; W the mass of the catalyst (g.); F the feed rate (mol./hr.) and x and b, mole fractions of xylene and benzene in the product. The above assumption is found to hold true because there is a good linear relationship between r_x/p_x and $(p^2_t - p_b p_x/K_d)/p_x$, as is shown in Fig. 8. The k_d values at 1 atm. of partial pressure of the feed are listed in

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[24] L. N. Johnson and K. N. Watson, *Natl. Petrol. News, Tech. Sec.*, (8) 9 (1946).

[25] E. Echigoya, T. Watanabe and K. Morikawa, 16th Annual Meeting of Chemical Society of Japan, Tokyo, 1963.

[26] K. Tarama, S. Teranishi, K. Hattori and T. Hosoi, ibid.

[27] T. Amemiya, E. Tsunetomi, E. Nakamura and T. Nakazawa, *J. Japan Petrol. Inc.* (*Sekiyu Gakkai Shi*), 3, 813 (1960).

[28] T. Amemiya, E. Tsunetomi, E. Nakamura, T. Nakazawa, M. Shimizu and H. Chiba, ibid., 3, 988 (1960).

Table IV. Apparent rate constants and selectivity

Partial pressure of the feed: 1 atm. E_a: apparent activation energy (kcal./mol.)
P: Pre-exponential factor

Catalyst	Reaction temp. °C	Apparent rate constants: Toluene disproportionation, $k_d \times 10^4$ (mol./hr. cat. g. atm^2) from Fig. 8	from Fig. 10	Toluene cracking $k_t \times 10^5$ (mol./hr. cat. g. atm.)	Xylene cracking $k_x \times 10^4$ (mol./hr. cat. g. atm.)	Selectivity S_t	S_x
Alumina-boria (10 wt. % boria)	450	2.9	3.1	1.0	4.2	29	0.69
	480	6.6	6.7	3.5	8.3	19	0.80
	510	13.7	13.9	8.6	14.7	16	0.93
	E_a	29.3		39.7	23.6		
	P	2.0×10^5		1.1×10^7	3.6×10^3		
		$k_d\times10^5$, from Fig. 10		$k_t\times10^6$	$k_x\times10^5$		
Silica-alumina* (commercial)	480	3.4		8.8	3.7	3.9	0.92
	510	6.2					
	540	10.9					
	E_a	24.0					
	P	2.8×10^2					

* k_d of fresh silica-alumina at 480°C: 1.75×10^{-4}
k_d of once regenerated silica-alumina at 480°C: 0.80×10^{-4}

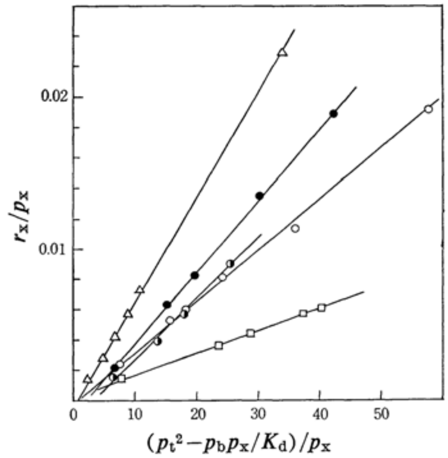

Fig. 8. Constancy of the retardation term of Eq. 1.
Reaction temperature (°C): △ 510, ○◑● 480, □ 450
Partial pressure (atm.): △○□ 1.0, ◑ 0.8, ● 0.6

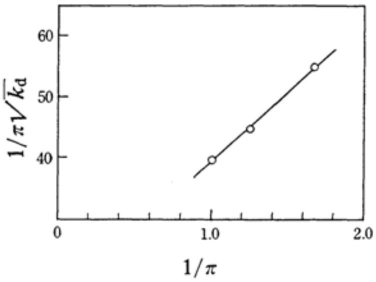

Fig. 9. Consistence of the rate expression derived from the Langmuir-Hinshelwood mechanism.

Table IV. From an examination of Eq. 1 for the reaction in the presence of benzene in the feed,[8] the following relation is found:

$$2K_t \doteqdot K_b + K_x$$
$$(K_t=0.48,\ K_b=0.42,\ K_x=0.63)$$

Accordingly, the rate constant, k_d, is expressed by the equation:

$$\left.\begin{aligned} &k_d = C_d/(1+\sum K_ip_i)^2 = C_d/(1+K_t\pi)^2 \\ \text{or}\quad &1/\pi = (\sqrt{C_d}/\pi\sqrt{k_d}) - K_t \end{aligned}\right\} \quad (3)$$

where π represents the partial pressure of the feed. The consistence of the above mechanism was verified by a linear relationship between $1/\pi$ and $1/\pi\sqrt{k_d}$ for the reaction at 480°C, as is illustrated in Fig. 9, and the mean value of K_t was obtained. The numerical expression of the disproportionation of toluene is as follows:

$$r_d = \frac{34.9\exp(-7400/T)}{\{1+4.12\times10^{-6}\pi\exp(9060/T)\}^2} \times (p_t^2 - p_bp_x/K_d)$$

(mol./hr. g. cat.), $T=723$ up to 783°K.

The mean value of the heat of the adsorption of reactants, 18 kcal./mol.

The apparent activation energy, 14.7 kcal./mol.

The relation between the time factor (W/F) and the mole fraction of xylene in the product (x) is described approximately by an integrated expression:

$$W/F = -\{\ln(1-mx)\}/n \qquad (4)$$

when m and n denote constants when the

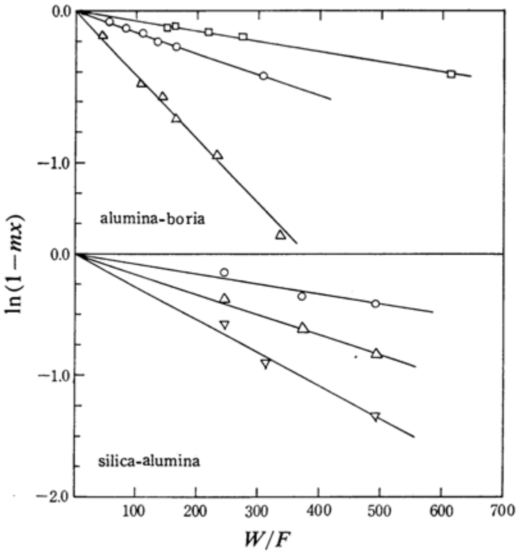

Fig. 10. Consistence of the integrated expression of Eq. 4 with experimental results at 1 atm. of partial pressure of the feed.

Alumina-boria	°C	m	$n\times10^3$	Silica-alumina	°C	m	$n\times10^4$
-□-	450	4.2	0.66	-○-	480	5.0	0.84
-○-	480	4.2	1.41	-△-	510	5.0	1.54
-△-	510	6.0	4.16	-▽-	540	5.0	2.72

reaction temperature is fixed. The consistency of Eq. 4 with the results of the reactions over alumina-boria and a commercial silica-alumina is shown in Fig. 10, where the optimum values of the constant, *m*, are also given. Equations 2 and 4 give the following relation:

$$\{\mathrm{d}x/\mathrm{d}(W/F)\}_{WF\rightarrow0}=n/m=k_\mathrm{d}/2 \qquad (5)$$

Table IV demonstrates the good accordance of k_d values calculated from Eq. 5 with those calculated from Eq. 2.

In the next place, the selectivity of the disproportionation is to be discussed. The following expression is derived from Eq. 2:

$$\{(1-\mathrm{d}x/\mathrm{d}b)/2\}(p^2{}_\mathrm{t}-p_\mathrm{b}p_\mathrm{x}/k_\mathrm{d})/p_\mathrm{x}$$
$$=(1/S_\mathrm{x})+(1/S_\mathrm{t})(\mathrm{d}x/\mathrm{d}b)(p_\mathrm{t}/p_\mathrm{x}) \qquad (6)$$

where $S_\mathrm{t}(=k_\mathrm{d}/k_\mathrm{t})$ and $S_\mathrm{x}(=k_\mathrm{d}/k_\mathrm{x})$ are defined as the selectivities of the disproportionation to toluene cracking and to xylene cracking respectively. Since $\mathrm{d}x/\mathrm{d}b$ can be calculated graphically, the numercal values of S_t and S_x are obtained by plotting the left term of Eq. 6 against $(\mathrm{d}x/\mathrm{d}b)(p_\mathrm{t}/p_\mathrm{x})$. The linear relationship of Eq. 6 is shown in Fig. 11. The values of S_t and S_x are calculated and listed in Table IV. It may be concluded that both the selectivity and the activity of alumina-boria are much higher than those of the commercial silica-alumina. The lower activity of the latter may be due principally to a higher tendency of coke fomation as well as to a lower concentration of active centers. The difference between the apparent activation energy of toluene cracking and that of xylene cracking, which are given in Table IV, suggests that the cracking reactivity is affected by the basicity of the aromatic nucleus.

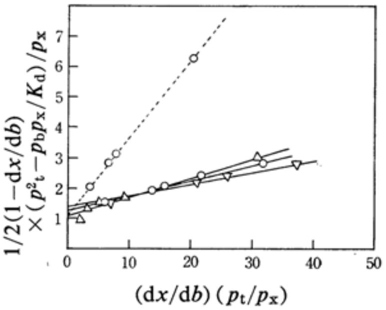

Fig. 11. Linear relationship between the left term of Eq. 6 with $(\mathrm{d}x/\mathrm{d}b)(p_\mathrm{t}/p_\mathrm{x})$.
Reaction temp. (°C): △ 510, ○ 480, ▽ 450.
——: Alumina-boria
----: Silica-alumina

The Decrease in Activity upon Coke Formation.—The toluene conversion of the disproportionation decreased with the length of the run and approached a constant value asymptotically, as is shown in Fig. 12. A carbon deposit on alumina-boria caused by the subsequent cracking reactions was observed, but regeneration could be easily accomplished by burning off the coke with air, giving the original activity. It may probably be concluded that a carbonaceous material covers the active

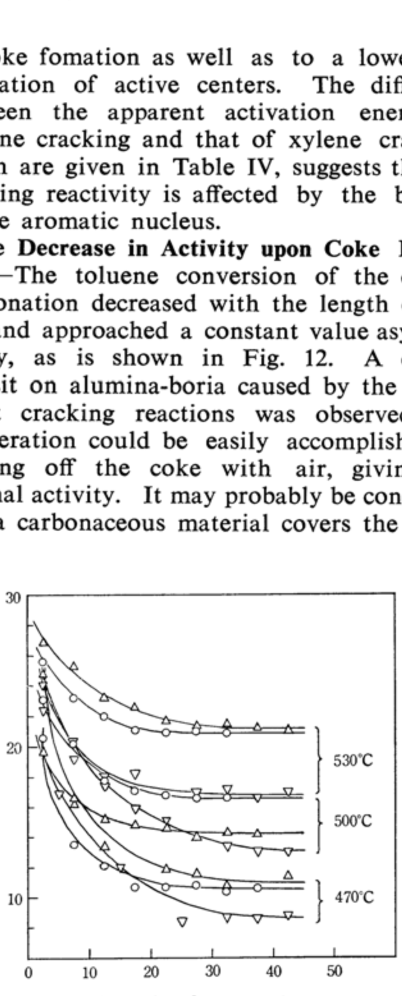

Fig. 12. Decrease in the activity of toluene disproportionation over the alumina-boria catalyst (15 wt. % boria).
Mass of catalyst: 5.0 g., ○ fresh, △ regenerated once, ▽ twice.
Feed rate: ○, △ 0.0568 mol./hr., ▽ 0.0660 mol./hr.

centers of the catalyst and lowers the activity.[29-31] Assuming that the concentration of active sites decreases in proportion to the amount of coke produced by the cracking of toluene and xylene, the following expression is given, taking into account the facts that the cracking of benzene is negligible and that the concentration of active centers is approximately proportional to the toluene conversion:

$$q=q_0\left\{1-\phi F\int_0^\theta (b-x)\,\mathrm{d}\theta\right\} \qquad (7)$$

where q_0 is the initial toluene conversion; q, the toluene conversion at a given time of run (θ); ϕ, the deactivation coefficient; b and x, the mole fractions of benzene and xylene of the product at θ, and F, the feed rate of toluene. The term of the integration denotes the cumulative quantity of cracking up to θ. When it is replaced by the average mole fraction of benzene ($\bar{b}$) and xylene ($\bar{x}$) instead of b and x during each successive fraction of time ($\varDelta\theta$), the integration in Eq. 7 is expressed as a summation of the fractional terms. Assuming further that a stationary-state conversion, q_s, is reached at a certain length of run when the covering effect of the coke on the active sites approaches equilibrium, a relative activity, q/q_s, is given by the following equation:

$$\left.\begin{aligned} q/q_s&=R\{1-\phi F\textstyle\sum(\bar{b}-\bar{x})\varDelta\theta\} \\ R&=q_0/q_s \end{aligned}\right\} \qquad (8)$$

The linear relationship between q/q_s and $F\sum(\bar{b}-\bar{x})\varDelta\theta$ is shown in Fig. 13. Since the deactivation coefficient and the relative activity, R, were approximately constant at a given reaction temperature, irrespective of either the regeneration of the catalyst or the change in the feed rate, the above interpretation of the decrease in activity seems to be analytically proved. If the ϕ coefficient is proportional to the adsorption equilibrium constant of the contaminant, a 4.2 kcal./mol. value is obtained for the apparent heat of its adsorption. The change in the ϕ values with the reaction temperature may be caused by the difference in the mechanism of the coke formation.[31] From a similar analysis of decrease in the activity of alumina-boria catalysts of different compositions, the relationship between the acidity and the initial activity, which is given as the product of q_s and R, is confirmed to be almost analogous to the correlation between the activity of the "equilibrated" catalyst and its acidity.[11]

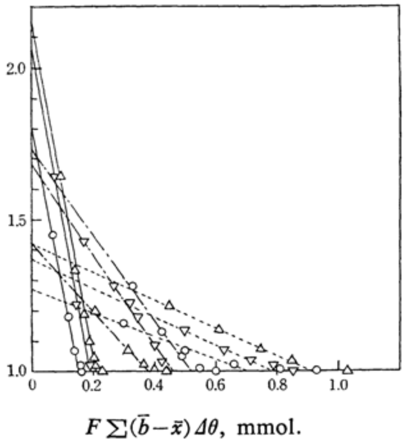

Fig. 13. Relation between the relative activity (q/q_s) and the cumulative amount of cracking ($F\sum(\bar{b}-\bar{x})\varDelta\theta$). See Fig. 12 for symbols. Reaction temp. (°C): —— 470, —·—· 500, ---- 530

		○	△	▽
470°C	R	1.8	2.2	2.1
	ϕ	2.9	2.6	2.8
500°C	R	1.7	1.4	1.7
	ϕ	0.82	0.76	0.90
530°C	R	1.3	1.4	1.4
	ϕ	0.30	0.33	0.33

The Isomerization of Xylene.—In the course of the isomerization of xylene, toluene and trimethylbenzene were produced simultaneously. Since the amount of benzene produced was negligible under the conditions of this study, only the disproportionation of xylene was taken into consideration as a side reaction.

TABLE V. RATE CONSTANTS OF XYLENE ISOMERIZATION OVER THE ALUMINA-BORIA CATALYST (15% BORIA, η-ALUMINA FOR BASE) AT 420 TO 480°C

Rate constant of xylene isomerization,
$k_{ij}=k'_{ij}/(1+\pi K_x)$, (mol./hr. cat. g. atm.)
Rate constant of xylene disproportionation,
$k_d=k'_d/(1+\pi K_x)^2$, (mol./hr. cat. g. atm²)

	Rate constant (T: °K)	Activation energy kcal./mol.
k'_{om}	28.4 exp(−4758/T)	9.46
k'_{op}	0.204 exp(−2258/T)	4.49
k'_{mo}	22.6 exp(−4954/T)	9.84
k'_{mp}	0.499 exp(−2218/T)	4.41
k'_{po}	2.05 exp(−3736/T)	7.42
k'_{pm}	7.95 exp(−3671/T)	7.29
k'_d	87.3 exp(−6302/T)	12.52
K_x*	0.0426 exp(1585/T)	3.15**

* K_x denotes the average adsorption equilibrium constant of the reactants.

** The value represents the average heat of adsorption of the reactants.

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[29] W. G. Appleby, J. W. Gibson and G. M. Good, Div. Petrol. Chem., Am. Chem. Soc., New York (Sept. 1960), 5, No. 4, B.

[30] E. M. Gladrow and C. N. Kimberlin, Jr., ibid., B-79.

[31] D. J. Wynnermen, ibid.

Assuming that both the rate of the isomerization and that of the disproportionation are controlled by surface reactions between adsorbed xylene molecules, the overall rate of the isomerization for the xylene isomers may be described by following expressions:

$$\left.\begin{aligned}
&\text{The rate of conversion of } o\text{-xylene:}\\
&\quad r_{\mathrm{o}}=-\mathrm{d}o/\mathrm{d}(W/F)=\pi\{(k_{\mathrm{om}}+k_{\mathrm{op}})o\\
&\qquad -k_{\mathrm{mo}}m-k_{\mathrm{po}}p\}+\pi^2k_{\mathrm{d}}ox\\
&\text{The rate of conversion of } m\text{-xylene:}\\
&\quad r_{\mathrm{m}}=-\mathrm{d}m/\mathrm{d}(W/F)=\pi\{(k_{\mathrm{mo}}+k_{\mathrm{mp}})m\\
&\qquad -k_{\mathrm{om}}o-k_{\mathrm{pm}}p\}+\pi^2k_{\mathrm{d}}mx\\
&\text{The rate of conversion of } p\text{-xylene:}\\
&\quad r_{\mathrm{p}}=-\mathrm{d}p/\mathrm{d}(W/F)=\pi\{(k_{\mathrm{po}}+p_{\mathrm{pm}})p\\
&\qquad -k_{\mathrm{op}}o-k_{\mathrm{mp}}m\}+\pi^2k_{\mathrm{d}}px\\
&\text{The rate of disproportionation of xylene:}\\
&\qquad r_{\mathrm{d}}=-\mathrm{d}x/\mathrm{d}(W/F)=\pi^2k_{\mathrm{d}}x^2\\
&\text{or}\qquad (1/x)-1=\pi^2k_{\mathrm{d}}(W/F)\\
&\qquad k_{\mathrm{ij}}=k'_{\mathrm{ij}}/(1+\pi K_{\mathrm{x}})\\
&\qquad k_{\mathrm{d}}=k'_{\mathrm{d}}/(1+\pi K_{\mathrm{x}})^2\\
&\qquad x=o+m+p
\end{aligned}\right\}\quad(9)$$

where o, m, p denote mole fractions of o-, m-, p-xylene in the product; k'_{ij}, the rate constant of the isomerization of the i-isomer to the j-isomer; k'_{d}, the average rate constant of the disproportionation of xylene isomers; π, the partial pressure of the total reactants, which is almost identical to that of the feed; K_{x}, the average adsorption equilibrium constant of the reactants; W, the mass of the catalyst, and F, the feed rate. The sum of k_{om} and k_{op} was obtained numerically from the initial rate of o-xylene conversion. The linear relationship between $1/\pi$ and $1/\pi(k_{\mathrm{om}}+k_{\mathrm{op}})$ gave the numerical values of $(k'_{\mathrm{om}}+k'_{\mathrm{op}})$ and K_{x}. All the constants in Eq. 9 were determined by a similar analysis searching for the initial rates of conversion of other isomers and by using the integrated formula of the disproportionation.[9] Table V represents the numerical expressions of the rates of isomerization and disproportionation. A comparison between the equilibrium constants of isomerization calculated from thermodynamic data[32] and those

TABLE VI. EQUILIBRIUM CONSTANTS OF XYLENE ISOMERIZATION CALCULATED FROM THERMODYNAMIC DATA

Reaction temp., °C	K_{pm}*	K_{om}	K_{op}
420	2.22(1.96)**	2.15(1.73)	0.965(0.886)
450	2.22(2.13)	2.10(1.50)	0.946(0.706)
480	2.22(2.32)	2.06(1.71)	0.928(0.737)

* K_{ij} denotes the equilibrium constant of isomerization of the i-isomer to the j-isomer.

** The value in parentheses was calculated from experimental data.

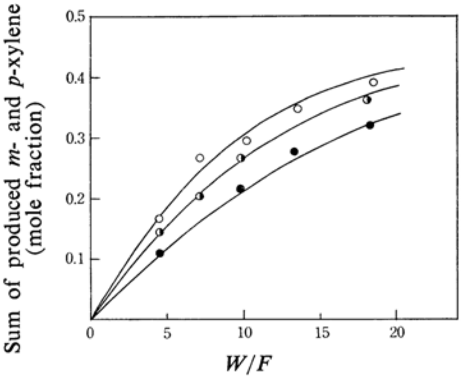

Fig. 14. Isomerization of o-xylene at 480°C over the alumina-boria catalyst (15 wt. %, η-alumina for base).
Partial pressure of the feed (atm.): ○ 1.00, ◑ 0.75, ● 0.50
——: Calculated from Eq. 10

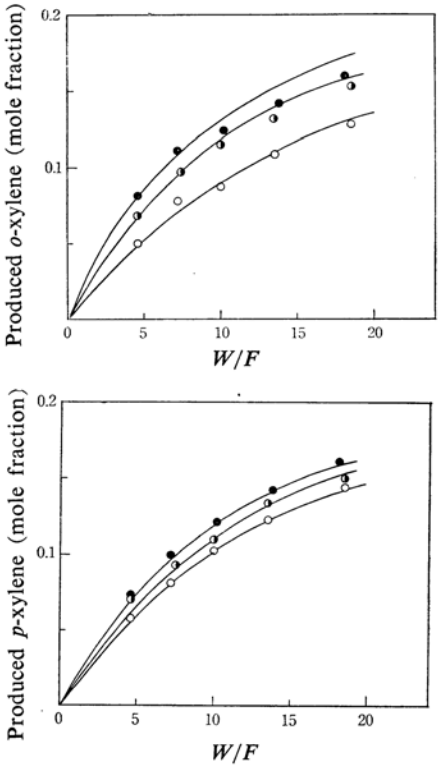

Fig. 15. Isomerization of m-xylene at 1 atm. of partial pressure of the feed.
Reaction temp. (°C): ○ 420, ◑ 450, ● 480
——: Calculated from Eq. 10

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[32] W. J. Taylor, D. D. Wagman, M. G. Williams, K. S. Pitzer and F. D. Rossini, *J. Research Nat. Bur. Standards*. 37, 95 (1946).

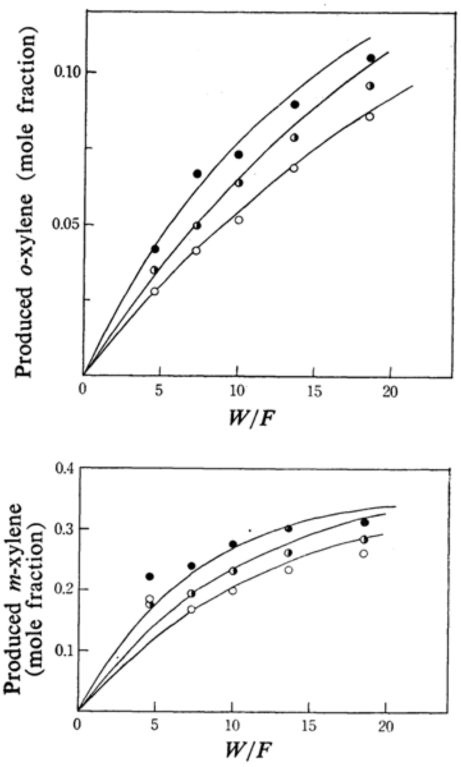

Fig. 16. Isomerization of p-xylene at 1 atm. of partial pressure of the feed.
Reaction temp. (°C): ○ 420, ◑ 450, ● 480
——: Calculated from Eq. 10

obtained by the experiment is shown in Table VI.

Amemiya and his co-workes[27,28] reported that the rate of xylene isomerization over a silica-alumina catalyst may be described by expressions similar to those in Eq. 9 except for the terms of the subsequent disproportionation. The integrated formula derived by them, however, was applicable only to such isomeric compositions as were not far from equilibrium. In the present study, the following integrated expressions are proposed for a wide range of the isomeric composition, (they include the subsequent disproportionation):

$$\left.\begin{aligned} \ln\{(o_0-o_e x)/(o-o_e x)\} &= \alpha(W/F) \\ \ln\{(m_0-m_e x)/(m-m_e x)\} &= \beta(W/F) \\ \ln\{(p_0-p_e x)/(p-p_e x)\} &= \gamma(W/F) \end{aligned}\right\} \qquad (10)$$

where o_0, m_0, p_0 are initial mole fractions of xylene isomers in the feed; o_e, m_e, p_e, equilibrium mole fractions of the isomers, and α, β, γ, the constants which are determined by a comparison of Eq. 9 with the differentiated forms of Eq. 10. The experimental data are very consistent with the expression of Eq. 10, as is shown in Figs. 14, 15 and 16.

Transethylation between Benzene and Diethylbenzene. — The reaction was carried out at 450°C, and ethylbenzene was produced with a negligible amount of toluene and gaseous products. The results are kinetically described by the following numerical rate expression, which is derived from the Langmuir-Hinshelwood mechanism:[10] the rate of formation of ethylbenzene at 450°C (mol./hr. cat. g.):

$$r = \mathrm{d}x/\mathrm{d}(W/F) = \frac{0.281(p_b p_d - p^2{}_e/K)}{(1+2.76p_b+11.85p_e+1.58p_d)^2} \qquad (11)$$

where x denotes the mole fraction of ethylbenzene in the product; p_b, p_e, p_d, the partial pressures (atm.) of benzene, ethylbenzene and diethylbenzene; W, the mass of the catalyst (g.), and F, the feed rate (mol./hr.). Since any side reactions can be neglected, Eq. 11 is easily integrated. The results are very consistent with the observed data, as is shown in Fig. 17, where the experimental finding of the reaction over a synthetic silica-alumina is also given for the sake of comparison. The acitivity of the silica-alumina was less than that of the alumina-boria. This is probably due to the lower concentration of active sites in the former.

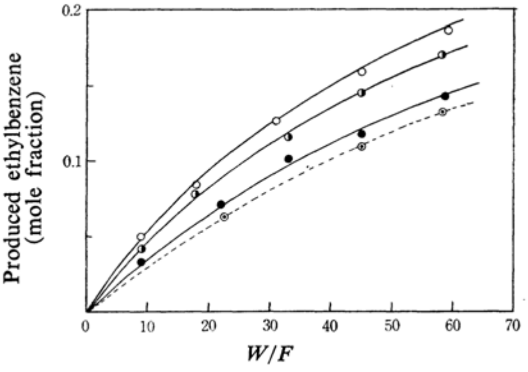

Fig. 17. Transethylation between benzene and diethylbenzene over the alumina-boria catalyst (15 wt. % boria, η-alumina for base) at 450°C using an equimolecular mixture as the feed.
Partial pressure of the feed (atm.): ○⊙ 1.00, ◑ 0.75, ● 0.50
——: Calculated from integrated expression of Eq. 11
----: Activity of a synthetic silica-alumina catalyst (50 wt. % SiO_2)

Summary

This study has aimed to secure an optimum means for the preparation of an alumina-boria catalyst by a systematic examination of the relationship between the physical characteristics of the catalyst and its activity, and to clarify

the mechanism of the development of activity on the basis of the experimental evidence about the chemical interaction of alumina with boric acid and about the chemical structure of the catalyst. The applicability of the catalyst has been studied kinetically for some specific reactions relating to the transalkylation of aromatic compounds. It has been found that alumina-boria shows a higher activity for these reactions than does silica-alumina.

The results and conclusion may be summarized as follows:

I) Boric acid is dehydrated to produce metaboric acid as a probable intermediate and reacts with an active alumina at about 130°C with little disturbance of the crystal structure of alumina, and effective acidic centers are produced. Most of the acid centers are of the Brönsted type. Alumina-boria does not show any definite chemical structure characteristic of aluminum borates, such as $9Al_2O_3 \cdot B_2O_3$, $2Al_2O_3 \cdot B_2O_3$ or $Al_2O_3 \cdot B_2O_3$. It is suggested that such a bond as Al–O–B–O–Al may be formed between surfaces of the crystal structure of alumina and may result in acidic centers.

II) The catalytic activity of toluene disproportionation shows a good correlation with the Brönsted acidity. This is well compatible with the likely theory that the reaction proceeds via a carbonium ion mechanism.

III) The activity of the disproportionation is considerably affected by the structure of the alumina used as the catalyst base as well as by the boria content of the catalyst. The catalyst prepared from η-alumina shows a higher activity than that from χ-alumina, while α-alumina does not give an active catalyst because of its poor reactivity with boric acid. A rise in the crystallinity of alumina lowers the reactivity. Excessive boria reduces the catalytic activity. An effective catalyst for the transalkylation of aromatic compounds can be obtained when alumina-boria is calcined above 400°C.

IV) The results of such reactions as the disproportionation of toluene, the isomerization of xylene and the transethylation between benzene and diethylbenzene can be well interpreted kinetically by assuming that the rates of these reactions are controlled by surface reactions between adsorbed molecules of the reactants.

V) In the disproportionation of toluene, a decrease in the activity of the catalyst with the length of the run was observed. This phenomenon can be explained analytically by taking into account the fact that some contaminant such as the carbonaceous material, which is produced by side reactions (cracking of toluene and xylene), covers effective sites of the catalyst.

VI) It seems to be due essentially to the higher concentration of active sites in alumina-boria that its activity of the transalkylation of aromatic compounds is higher than that of silica-alumina.

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