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The Formation of High-boiling By-products in the Isomerization and Disproportionation of *m*-Xylene over a Silica-alumina Catalyst under Pressure

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Continuous liquid-phase isomerization and disproportionation reactions over silica-alumina catalysts were carried out using *m*-xylene with varying concentration of water. The reactions were conducted at 290°C and 400°C under a pressure of 300 kg/cm^2. The results showed that the concentration of water required to attain a maximum activity for the isomerization was higher than that needed for the disproportionation reaction. The high-boiling by-products produced at 400°C comprized 2—5 per-cent of the weight of the total products, and the main component, polymethyldiphenylmethane, amounted to 70—80 per-cent of the by-products. The yield of polymethyldiphenylmethane was linearly correlated with that of toluene. This result appears to suggest that the disproportionation reaction and the polymethyldiphenylmethane formation proceed at a common active site and through the same intermediate.

In an earlier paper[1] the present authors reported that, in the liquid-phase isomerization of *m*-xylene, a silica-alumina catalyst revealed higher activity than in the vapor-phase reaction; moreover, even after 20 days no practical decline in the activity was observed. This superior ability of the catalyst in the liquid phase can be ascribed to the cleaning effects of the liquid reactant: in the liquid-phase reaction, the high-boiling by-product which, in the vapor-phase reaction, causes the activity to diminish due to its strong adsorptivity on the surface sites, is successively dissolved into the reactant; therefore, more surface sites are available for the isomerization.

As was shown in an earlier paper,[1] some components in the high-boiling by-product exhibit a temporary inhibiting effect, and these seem to be transformed into higher boiling compounds which exert a permanent poisoning effect on the catalytic activity. Hence, the decline in activity can not be avoided even in the liquid phase when the high-boiling by-product is produced to a great extent. On the basis of such considerations, it will be valuable, for the sake of the improvement of the catalyst life, to discover some means to reduce the yield of the high-boiling by-product.

The liquid-phase reaction can be characterized from another point of view—the yields of the high-boiling by-product can be measured rather quantitatively. Therefore, for the purpose of examining the possibility of reducing the high-boiling by-product or the disproportionation reaction products in the isomerization of *m*-xylene, the correlation between the yield of the high-boiling by-product and that of the disproportionation product, as well as the correlation between the yield of the isomerization product and that of the disproportionation product, will be studied in this paper. Practically, the correlations were studied over silica-alumina catalysts calcined at various temperatures by using *m*-xylene containing various amounts of water. It is well-known that a small amount of water influences the catalytic activity of silica-alumina.[2,3]

Experimental

The catalysts employed were two kinds of silica-alumina: one (I) was synthesized from aluminum isopropoxide and ethyl silicate,[4] while the other (II) was Nikki N633L. Both of these catalysts were calcined at 400°C or at 600°C for 20 hours. The equipment and the procedure for carrying out the continuous liquid-phase xylene isomerization under a high pressure were shown in previous papers.[1,5] In this study, all the experiments were carried out at a contact time (W/F) of 0.5 g-cat. h/g under a pressure of 300 kg/cm^2.

The reactant *m*-xylene (produced by Japan Gas Chemical Co. Inc.) was 99.6% pure and contained 100—130 ppm of water. Therefore, the concentration of water in the *m*-xylene was adjusted to the desired extent by drying with metallic sodium or calcium chloride and was determined by means of the Kaal-Fisher method.

The product was analyzed by gas chromatography. Two kinds of columns were used: one was 4 m in length, 1 mm in dia., and was packed with 5 per-cent Benton 34+DIDP

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[1] H. Takaya, N. Todo, T. Hosoya, T. Minegishi, M. Yoneoka, and H. Ōshio, This Bulletin, **44**, 2296 (1971).

[2] A. Ozaki, "Catalyst Handbook," ed. by A. Ozaki, K. Tamaru, K. Tanabe, and S. Nishimura, Chijinshokan, Tokyo, Japan. (1967) p. 204.

[3] T. Iwasaki and R. Hatta, *Kogyo Kagaku Zasshi*, **63**, 1975 (1960).

[4] S. Yamadaya and H. Uchida, *Tokyo Kogyo Shikenjo Hokoku*, **61**, 254 (1966).

[5] H. Takaya, N. Todo, T. Hosoya, T. Minegishi, and M, Yoneoka, *Kogyo Kagaku Zasshi*, **73**, 1831 (1970).

on diasolid L (100—200 mesh), while the other was 2 m in length, 3 mm in dia. and was packed with 20 per-cent silicone grease on celite 545.

The high-boiling by-product was separated by distilling the product at 100°C under a reduced pressure of 5 mmHg. Its composition was determined from the parent peaks of the mass spectra obtained by means of a Hitachi double-beam mass spectrometer.

Results and Discussion

Under the liquid-phase reaction conditions, the silica-alumina catalyst pretreated at a moderate temperature showed a considerably high activity for the isomerization reaction.[1,5] Accordingly, in order to detect the effects of water content on the activity, the reaction had to be carried out at a low temperature of 290°C where the equilibria among xylene isomers had not been established. On the other hand, at this temperature the rate of the production of the high-boiling compounds was very slow. Hence, in order to get information about the high-boiling by-product formation, the reaction was carried out at a higher temperature of 400°C, where measurable amounts of these compounds could be obtained.

3.1 Results at the Reaction Temperature of 290°C. The effects of water on both the isomerization and the disproportionation reaction were studied by using the II catalyst calcined at 600°C; the results are shown in Figs. 1-a, 2-a, and 3-a. In addition, it is known that the yield of toluene is approximately equal to that of trimethylbenzene at the reaction temperature of 290°C; hence, the yield of toluene can be considered as the disproportionation activity.[5] In these figures, the yield for neither the isomerization nor the disproportionation reaction in the first sample taken after 4 hours' reaction was obtained with a good reproducibility. As will be described below, however, this study aimed to follow only the manner of variation in the yields of the isomerization products and the disproportionation-reaction products with time. Thus, the lack of the reproducibility of the first yields of the products was not taken into account. The figures show that when the concentration of water in *m*-xylene was changed, the yields of the isomerization products varied with time in a different manner from those of the disproportionation. This fact suggests that different active sites may be available for the two reactions. This consideration was more clearly supported by the result shown in Fig. 1-b: when the reactant was changed from the *m*-xylene containing water below 5 ppm to the *m*-xylene containing 100—130 ppm, the yields of the isomerization products were recovered to about 50 per-cent of the initial ones, while the yield of the disproportionation product was decreased monotonously.

The variations in the activities for the isomerization and the disproportionation with the reaction time, as are shown in Figs. 1—3, appear to be attributable to the gradual adsorption of water in the reactant *m*-xylene in the cases of Figs. 2-a and 3-a, and to the deactivation due to the adsorption of undesirable high-boiling by-

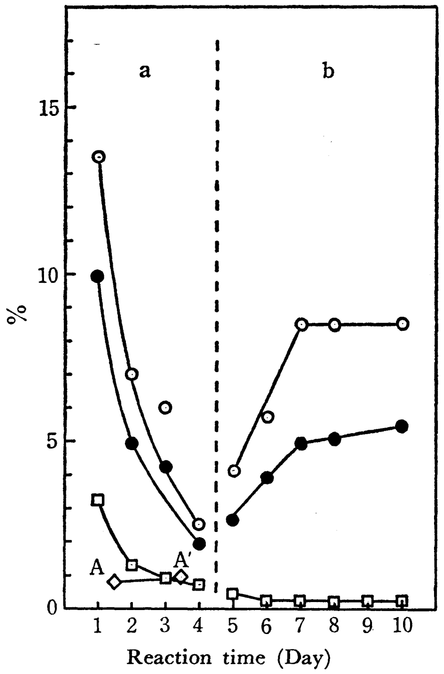

Fig. 1. Variation of activity with reaction time.
Catalyst: II. Calcining temperature of the catalyst: 600°C. Reaction temperature: 290°C. Concentration of water in *m*-xylene: below 5 ppm and 100—130 ppm in the regions designated by a and b respectively.
○: *p*-Xylene. ●: *o*-Xylene. □: Toluene.
◇: High-boiling by-products.

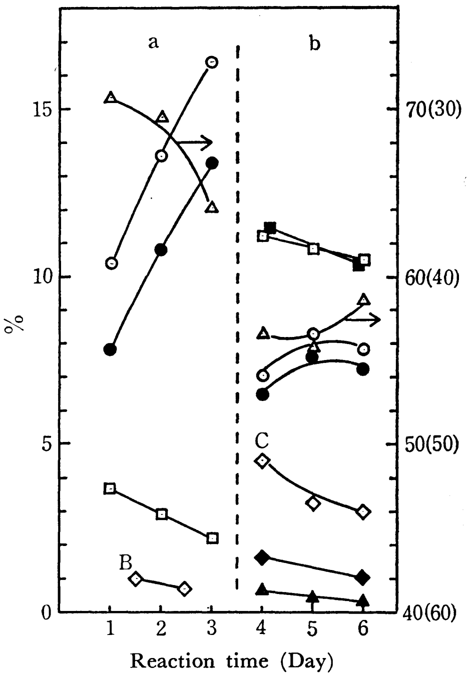

Fig. 2. Variation of activity with reaction time.
Catalyst: II. Calcining temperature of the catalyst: 600°C. Reaction temperature: 290°C and 400°C in the regions designated by a and b respectively. Concentration of water in *m*-xylene: 20—30 ppm. The figures in parentheses along the right ordinate show the conversions of *m*-Xylene: the conversion = 100% − an amount of unreacted *m*-xylene %.
△: *m*-Xylene. ○: *p*-Xylene. ●: *o*-Xylene.
□: Toluene. ■: Trimethylbenzene. ▲: Benzene.
◆: Tetramethylbenzene. ◇: High-boiling by-products.

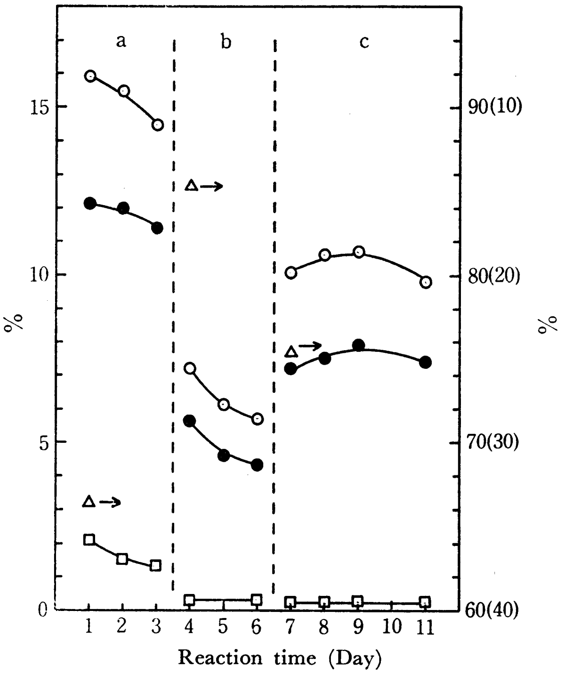

Fig. 3. Variation of activity with reaction time.
Catalyst: II. Calcining temperature of the catalyst: 600°C. Reaction temperature: 290°C. Concentration of water in *m*-xylene: 100—130 ppm and 20—30 ppm in the regions designated by a and c respectively. In the region designated by b, 1000 ppm of methanol was added to *m*-xylene.
△: *m*-Xylene. ○: *p*-Xylene. ●: *o*-Xylene.
□: Toluene.

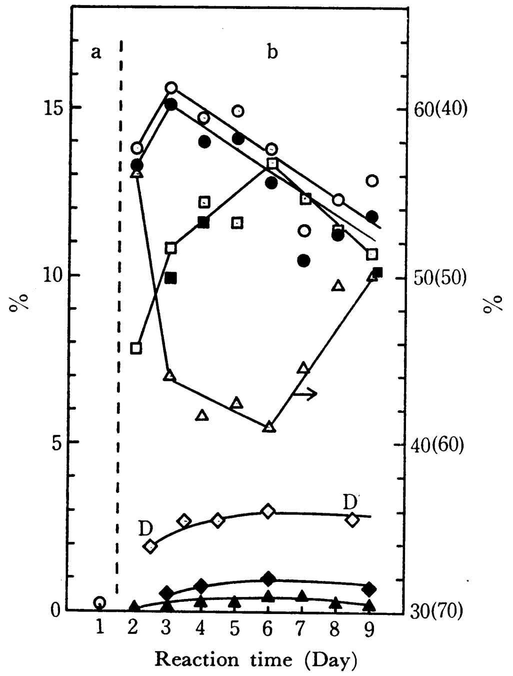

Fig. 4. Activity of Catalyst II.
Calcining temperature: 400°C. Reaction temperature: 290°C and 400°C in the regions designated by a and b respectively. Concentration of water in *m*-xylene: 20—30 ppm.
△: *m*-Xylene. ○: *p*-Xylene. ●: *o*-Xylene.
□: Toluene. ■: Trimethylbenzene. ▲: Benzene.
◆: Tetramethylbenzene. ◇: High-boiling by-products.

products in the case of Fig. 1-a. Also, Figs. 3-b and 3-c show the effects of the adsorption and desorption of water on the activities. In Fig. 3-b, methyl alcohol was decomposed to water and methyl ether. These results show that there was an amount of water adequate for the maximum activity for the isomerization, but that the activity for the disproportionation increased with a decrease in the concentration of water in *m*-xylene.

Figure 4-a illustrates that the II catalyst calcined at 400°C showed practically no activity in the two reactions. However, the I catalyst calcined at the same temperature revealed a low but measurable activity, as is shown in Fig. 5. This difference between the two catalysts may be related to the content of water in the catalysts, since the results obtained by the use of TGA and DTA showed that the dehydration of the II catalyst took place at a higher temperature than that of the I catalyst.

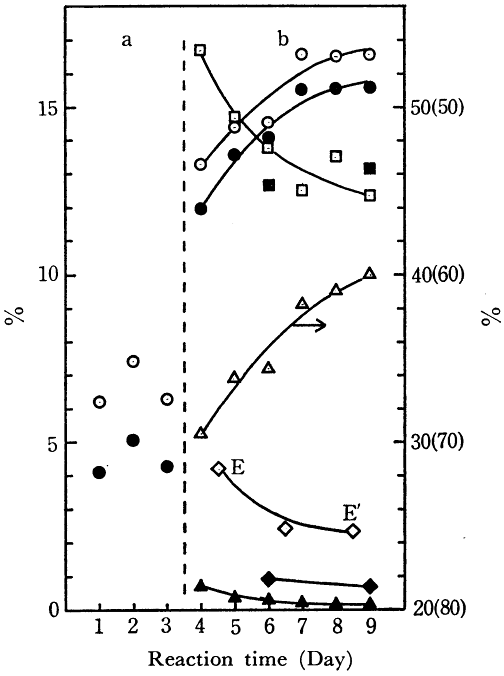

Fig. 5. Activity of catalyst I.
Calcining temperature: 400°C. Reaction temperatures: 290°C and 400°C in the regions designated by a and b respectively. Concentration of water in *m*-xylene: 20—30 ppm.
△: *m*-Xylene. ○: *p*-Xylene. ●: *o*-Xylene.
□: Toluene. ■: Trimethylbenzene. ▲: Benzene.
◆: Tetramethylbenzene. ◇: High-boiling by-products.

3.2 The Results at a Reaction Temperature of 400°C.

3.2.1 The Results Using II Catalyst: The results obtained at a reaction temperature of 400°C are shown in Figs. 2-b, 4-b, 6-b, and 7. These results can be divided into three groups, depending on the yields of the isomerization products and the disproportionation reaction products. In the first group (Figs. 6-b and 7), the equilibria among xylene isomers were established; also, the disproportionation products were produced in high yields. It can be said such results were obtained for the cases where the catalysts calcined at 600°C were used and where the reaction systems involved

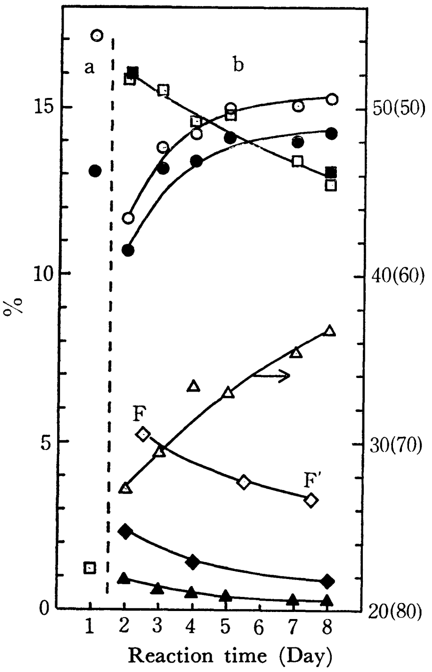

Fig. 6. Activity of catalyst II.
Calcining temperature: 600°C. Reaction temperatures: 290°C and 400°C in the regions designated by a and b respectively. Concentration of water in *m*-xylene: 100—130 ppm.
△: *m*-Xylene. ○: *p*-Xylene. ●: *o*-Xylene. □: Toluene. ■: Trimethylbenzene. ▲: Benzene. ◆: Tetramethylbenzene. ◇: High-boiling by-products.

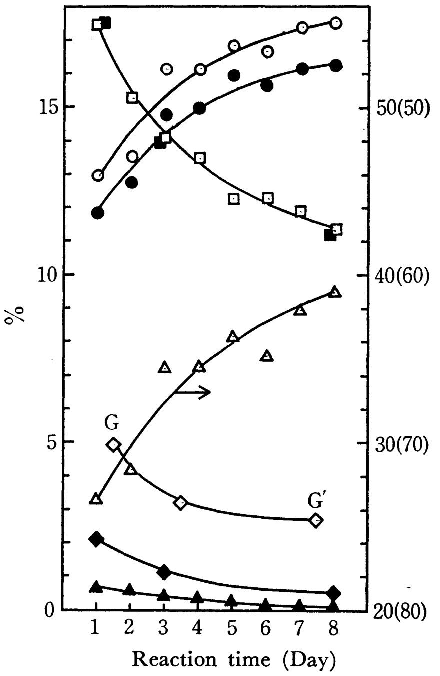

Fig. 7. Activity of catalyst II with using *m*-xylene containing 1000 ppm of methanol.
Calcining temperature of catalyst: 600°C. Reaction temperature: 400°C.
△: *m*-Xylene. ○: *p*-Xylene. ●: *o*-Xylene. □: Toluene. ■: Trimethylbenzene. ▲: Benzene. ◆: Tetramethylbenzene. ◇: High-boiling by-products.

comparatively high concentrations of water; the reactant *m*-xylene contained a high concentration of water or 1000 ppm of methyl alcohol. On the other hand, the characteristic feature of the second group (Fig. 2-b) is that the yield of the disproportionation-reaction product was higher than that of the isomerization product in spite of the low conversion of *m*-xylene. In this group, the equilibria among xylene isomers were not established. This feature can be seen more clearly by comparing Fig. 2-b (obtained at a reaction temperature of 400°C) with Fig. 2-a (obtained at a reaction temperature of 290°C); the yields of the isomerization products at a reaction temperature of 290°C were more than those of the disproportionation, though the conversion of *m*-xylene was approximately equal to that at a reaction temperature of 400°C. The results of Fig. 2 were obtained using a catalyst calcined at 600°C and *m*-xylene containing a low concentration of water. The third was a group which showed a medium activity (Fig. 4-b). This was the case where a catalyst calcined at 400°C for 20 hours was used. It seems that the relatively lower activity than that of the first group may result from the insufficiency of the dehydration of the catalyst; the pretreatment of the II catalyst at 400°C for 20 hours was insufficient for the catalyst to reveal a high activity. The increasing activity up to the fourth day appears to correspond to the increase in the extension of the dehydration.

3.2.2 The Results with Using I Catalyst: According to the yields of the isomerization products and the disproportionation-reaction products, it may be said that the results shown in Figs. 5-b and 8-b belong to the first group and the second group respectively. The I catalyst calcined at 400°C revealed a high activity, as is shown in Fig. 5, where the reactant *m*-xylene contained 20—30 ppm of water. This result differs from that with using the II catalyst calcined at 400°C (Fig. 4-b). This discrepancy in activity may also be attributed to the greater ease of the dehydration of the I catalyst. The results shown in Fig. 8-b, where the catalyst was calcined at 600°C and where the reactant, *m*-xylene, contained 20—30 ppm of water, are the same

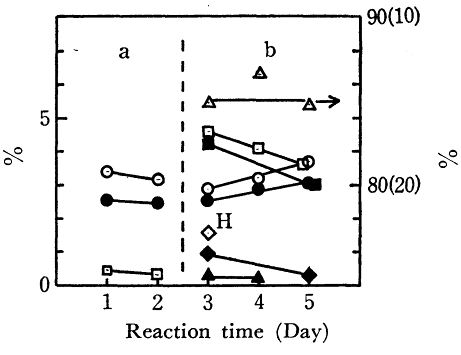

Fig. 8. Activity of catalyst I.
Calcining temperature of catalyst: 600°C. Reaction temperatures: 290°C and 400°C in the regions designated by a and b respectively. Concentration of water in *m*-xylene: 20—30 ppm.
△: *m*-Xylene. ○: *p*-Xylene. ●: *o*-Xylene. □: Toluene. ■: Trimethylbenzene. ▲: Benzene. ◆: Tetramethylbenzene. ◇: High-boiling by-products.

as those in Fig. 2-b.

3.3 High-boiling By-product. The product for 23 hours' operation (about 130 g) was distilled at a reduced pressure of 5 mmHg and at a temperature of 100°C; the residue thus obtained was regarded as comprising the high-boiling by-products. As is shown in Figs. 1—8, the yields of the high-boiling by-products were in the range of 2—5 per-cent and seemed to be correlated with the yields of toluene. However, as to the isomerization products, the correlation with the high-boiling by-products could not be examined because, in most of cases, the equilibria of the isomerization were established.

The decline in activity observed in most cases at the reaction temperature of 400°C might be attributed to the large yields of high-boiling by-products. Two per-cent of the weight of the by-products was sufficient to lower the catalyst activity.1)

The compositions of the high-boiling by-products were analyzed by means of a mass spectrometer under the conditions described in a previous paper.1) The mass spectra of the samples designated by A—H in Figs. 2—8 were observed; three representative spectra are shown in Fig. 9. It can be seen that all the spectra consist of three homologous series differing in mass number by 14, corresponding to the replacement of a hydrogen atom by a methyl group. The three series correspond to polymethylnaphthalene, polymethyldiphenylmethane, and polymethylanthracene. The compositions and the yields are shown in Table 1. This table shows that polymethyldiphenylmethanes amounted to 70—80 per-cent and were the main components of the high-boiling by-product at the reaction temperature of 400°C. In the case of the reaction at 290°C, tetramethyldiphenylmethane, the mass number of which is 224, was the main product, and the amount of anthracene was small.

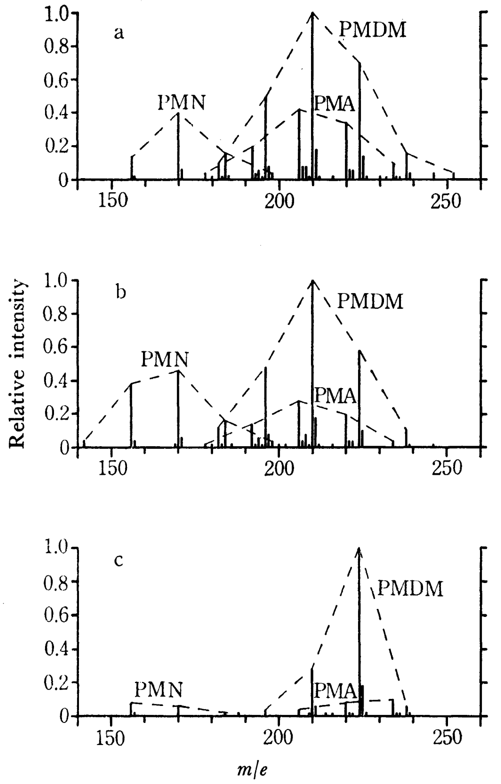

Fig. 9. Mass spectra of the high-boiling by-products.
These mass spectra were obtained at ionization voltages as low as 15 V in order to allow only the parent peaks of the components to appear.
a: Sample F shown in Figs. 6 and 10, and in Table 1.
b: Sample C shown in Figs. 2 and 10, and in Table 1.
c: Sample B shown in Figs. 2 and 10, and in Table 1.
PMN: Polymethylnaphthalene.
PMDM: Polymethyldiphenylmethane.
PMA: Polymethylanthracene or polymethylphenanthrene.

3.4 The Active Sites for the Isomerization and the Disproportionation. The results presented in Section 3.2 show that, at a reaction temperature of 400°C, the high activity for the isomerization and the disproportionation reaction was obtained under the reaction conditions of the first group, where an adequate amount of water existed in the reaction systems. This suggests that an adequate concentration of water is required to attain a maximum activity not only for the isomerization but also for the disproportionation reaction. However, considering the finding at 290°C that the activity for the disproportionation increased with a decrease in the concentration of water the required concentration for the disproportionation appears to be lower than that for the isomerization.

In connection with the active sites available for the isomerization, it has been generally accepted that the reaction is catalyzed by a protonic acid.6,7,8,9,10) The present results related with the effect of water concentrations on the isomerization activity really coincide with this view. As for disproportionation or transalkylation, however, the active sites proposed by several authors are not entirely consistent. From the correspondency of the catalytic activity to the Brønsted acidity, Izumi and Shiba11) concluded that the disproportionation of toluene over an alumina-boria catalyst proceeds mainly on protonic-acid sites. Matsumoto *et al.*8) reached the same conclusion with regard to the active sites for the disproportionation of *o*-xylene over a calcium-exchanged NaX-zeolite catalyst. On the other hand, according to Csicsery,9) the ratio of the isomerization to the transalkylation of 1-methyl-2-ethylbenzene over a silica-alumina catalyst increased with an increase in the water content of the reactant. They suggested, therefore, that transalkylation is catalyzed predominantly by a Lewis acid or by a protonic acid and Lewis acid pair.

If we assume that the disproportionation occurs at the protonic acid site, the present results can be interpreted as indicating that the acid strength of the site available for the disproportionation should be stronger than that for the isomerization, because the increasing concentration of water in the reaction system would reduce the mean acid strength due to the adsorption of water, which has a basic property. On the other

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6) V. C. F. Holm and A. Clark, *J. Catal.*, **2**, 16 (1963).

7) T. Iwasaki, *Waseda Daigaku Oyokagakukaiho*, **30**, 4 (1963).

8) H. Matsumoto and Y. Morita, *Bull. Japan Petroleum Institute*, **11**, 40 (1969). *Kogyo Kagaku Zasshi*, **70**, 1674 (1967), *ibid.* **71**, 1004 (1968), *ibid.* **71**, 1496 (1968).

9) S. M. Csicsery and D. A. Hickson, *J. Catal.*, **19**, 386 (1970).

10) J. W. Ward, *ibid.*, **17**, 355 (1970).

TABLE 1. THE YIELDS AND THE COMPOSITION OF HIGH-BOILING BY-PRODUCTS

Sample[a]		A	A′	B	C	D	D′	E	E′	F	F′	G	G′	H
Catalyst		II		II	II	II		I		II		II		I
Calc. temp of Cat. °C		600		600	600	400		400		600		600		600
React. temp °C		290		290	400	400		400		400		400		400
Concentration of water in m-xylene ppm		below 5		20–30	20–30	20–30		20–30		100–130		1000[g]		20–30
Yield[b], %	PMN[c]	0.1			1.0	0.2	0.3	0.7	0.2	0.8	0.3	0.9	0.2	0.1
	PMDM[d]	0.7	0.9	0.8	3.1	1.5	2.2	2.9	1.9	3.7	2.7	2.9	2.3	1.3
	PMA[e]				0.4	0.2	0.2	0.5	0.2	0.6	0.2	0.4	0.2	0.2
Composition[f], %	PMN	6	2	6	21	13	11	16	10	15	10	20	8	7
	PMDM	90	94	89	69	77	78	69	80	71	83	68	84	79
	PMA	4	4	5	8	9	9	12	9	12	6	10	7	12

a) These samples were shown also in Figs. 1—8 by the signs of A, A′,… and H. b) Ratios to total products.
c) Polymethylnaphthalene. d) Polymethyldiphenylmethane. e) Polymethylanthracene.
f) Compositions of high-boiling by-products. g) Concentration of methyl alcohol.

hand, if we assume that the disproportionation reaction would be catalyzed by a Lewis acid, the role of water may be interpreted as promoting the desorption of undesirable products, polymethyldiphenylmethanes, due to the strong affinity of water with the acid sites. Up to an adequate content of water for the disproportionation, the produced polymethyldiphenylmethanes are desorbed successively without any formation of higher condensation products; thus, the effective sites could be prevented from permanent poisoning. A further increase in the water content, however, may result in a decrease in the effective active sites.

In conclusion, a full designation of the active sites available for the disproportionation seems to be beyond our reach at present; thus, further investigations must be made from a different point of view.

3.5 High-boiling By-products and Toluene. As is indicated in Fig. 10, the yield of polymethyldiphenylmethane, the main component of the high-boiling by-products, shows an approximately linear relation with that of toluene. This appears to suggest that the disproportionation reaction and the polymethyldiphenylmethane formation proceed at a common active site and through the same intermediate. Therefore, it may be reasonable to think that the intermediate is similar to diphenylmethane, as is shown in Fig. 11. Lanewala[12] and Csicsery[13] proposed an intermediate similar to Fig. 11 for the transalkylation of alkylbenzenes over zeolite catalysts. Polymethyldiphenylmethanes seem to be produced by the release of a hydrogen molecule or methane from the intermediate.

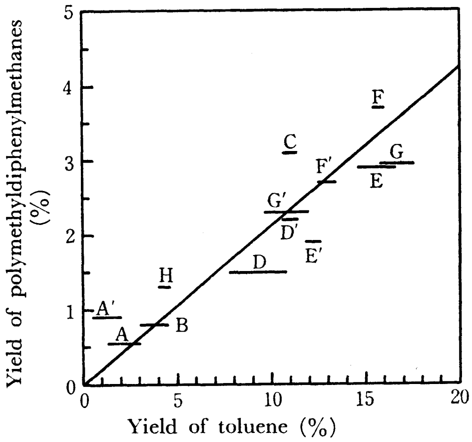

Fig. 10. Yield of polymethyldiphenylmethane versus that of toluene.
The letters indicate the samples shown in Table 1.
The width of the yield of toluene was caused by the fact that the deactivation occurred during 23 hr operation to obtain high-boiling by-products.

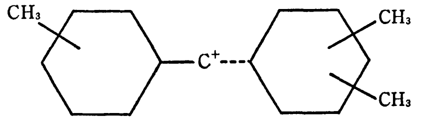

Fig. 11. A probable intermediate for the disproportionation reaction and the formation reaction of the polymethyldiphenylmethane.

As is shown in Fig. 9-c, tetramethyldiphenylmethane is the main component of the high-boiling by-product at the reaction temperature of 290°C. Considering the intermediate shown in Fig. 11, trimethyldiphenylmethane may be expected to be the main component at that reaction temperature, since the xylenes in the product amounted to more than 90 per-cent. This conflict can be resolved by considering the occurrence of a rapid exchange reaction between a reactant xylene and an aromatic ring of diphenylmethane.[14]

In addition, as is shown in Figs. 9-a and 9-b, the composition of the high-boiling by-product at 400°C was independent of the water concentration in m-xylene. In connection with the high-boiling by-products, another finding was that the product distribution of parent peaks of polymethylanthracene, which exert a stronger poisining effect on the catalyst activity than does diphenylmethane,[14] is similar to that of polymethyldiphenylmethane. This result leads us to think that polymethylanthracene would be formed dominantly from polymethyldiphenylmethane. However, poly-

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[11] A. Izumi and T. Shiba, *Nippon Kagaku Zasshi*, **84**, 699 (1963).

[12] M. A. Lanewala and A. P. Bolton, *J. Org. Chem.*, **34**, 3107 (1969).

[13] S. M. Csicsery, *ibid.*, **34**, 3338 (1969).

[14] H. Takaya, N. Todo, T. Hosoya, H. Ōshio, and T. Minegishi, This Bulletin, in press.

methylanthracene or polymethylphenanthrene formation may occur through polymethylnaphthalene, since a small amount of polymethylnaphthalene was found in the products.

On the basis of the suggested mechanism concerning the formation of high-boiling by-products, it may be concluded that, under reaction conditions or a reaction system where the disproportionation products are required to be produced in high yields, a decline in the catalytic activity is unavoidable.