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Cleaning Effects of the Reactant in the Liquid-phase Isomerization of *m*-Xylene over a Silica-Alumina Catalyst under Pressure

Haruo Takaya, Naoyuki Todo, Tadasuke Hosoya, Toshio Minegishi
Mikio Yoneoka,* and Hideki Ōshio**

The Government Chemical Industrial Research Institute, Tokyo, Mita, Meguro-ku, Tokyo
**Japan Gas-Chemical Company, Inc., Niigata Laboratory Enoki-cho, Niigata*
***The Research Laboratory, Central Glass Company, Ltd., Imafuku, Kawagoe-shi, Saitama*

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The activity of silica-alumina catalyst in the isomerization of *m*-xylene was measured at the temperatures of 290°C, 320°C, 380°C, and 430°C in the liquid phase under a pressure of 300 kg/cm^2. The observed activities were considerably higher than those in vapor-phase reactions, moreover even after 20 days practically no decline in the activity was observed except for the measurements at 430°C. This superior ability of the catalyst in the liquid phase can be ascribed to the cleaning effect of the liquid reactant: in the liquid-phase reaction the high-boiling by-product, which, in vapor-phase reactions, diminishes the activity because of its strong adsorptivity on the surface sites, is successively dissolved in the reactant; therefore, more surface sites are constantly available for the isomerization. This interpretation was substantiated by the following results: 1) when the reaction was operated in the liquid phase, about eighteen times as much high-boiling by-product was obtained as in the vapor phase; 2) the activity in the liquid-phase reaction was much higher than that in the vapor phase; 3) the decreased activity caused by the interruption of the flow was regenerable when the flow was resumed; 4) the addition of the high-boiling by-product to the reactant *m*-xylene resulted in a considerable decrease in the activity. In addition, the identification of the components in the high-boiling by-products was carried out by means of mass and NMR spectroscopic studies.

In earlier papers, the present authors reported on the effect of pressure on the equilibrium composition of xylene isomers¹⁾ as well as on the rate of the isomerization of *m*-xylene over a silica-alumina catalyst.²⁾ In these studies it was found that the silica-alumina catalyst revealed considerably higher activity in the liquid-phase reactions than in the vapor-phase reactions. Such an enhanced activity in the liquid-phase reactions can not be explained in terms of the increase in the coverage of xylenes on active sites, since the coverage is already high at atmospheric pressure.³⁾

It was presumed from the charactersistic coloration of the products that the enhanced activity in the liquid-phase reaction is caused by the cleaning effect of the liquid reactant; in the liquid-phase reaction, the high-boiling by-product, which, in the vapor-phase reaction diminishes the catalyst activity because of its strong adsorptivity on the surface sites, is successively dissolved in reactant liquid xylenes; therefore, more surface sites are constantly available for the isomerization reaction. The purpose of this study is to confirm the above presumption.

Experimental

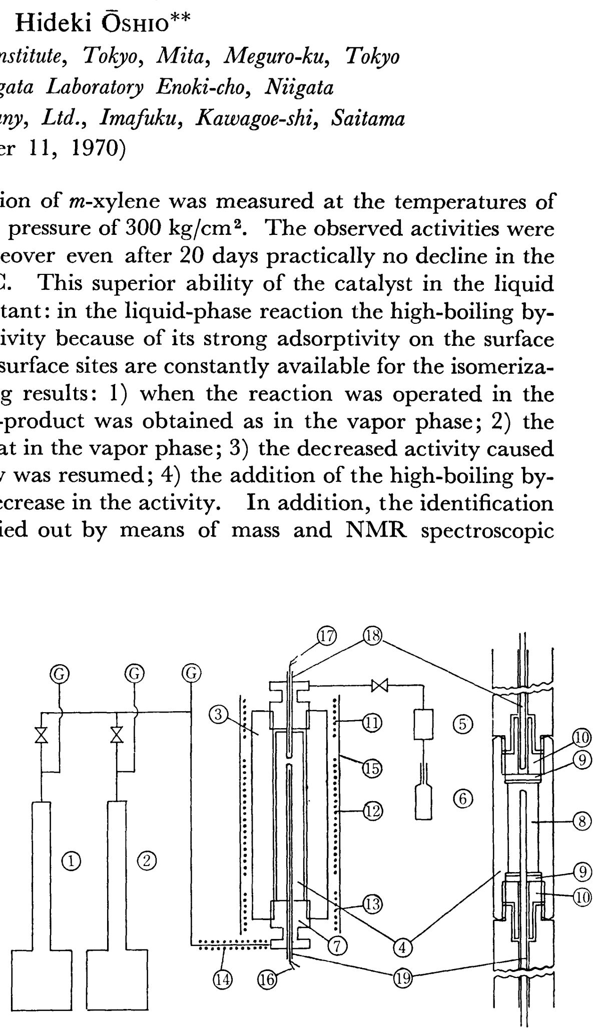

Fig. 1. The equipment.
1 and 2: Pumps for xylene. 3: Pressure vessel. 4: Reactor. 5: Pressure regulator. 6: Product receiver. 7: Lower flange. 8: Catalyst bed. 9: Porous sintered 18–8 stainless steel disk. 10: Gland nut. 11, 12, 13, and 14: Nichrome resistance wires. 15: Asbestos cloth. 16 and 17: Thermocouples. 18 and 19: 18–8 stainless steel pipes.

As is shown in Fig. 1, the equipment for carrying out continuous liqid-phase xylene isomerization under high pressure consisted of a pressure vessel, 3, containing a catalytic reactor, 4, and auxiliary equipment including pumps for xylene, 1 and 2, a pressure regulator, 5, and a product receiver, 6. All the equipment in contact with the process fluid was made of 18–8 stainless steel. The reactor placed on the lower flange, 7, of a pressure vessel, 1, had two porous sintered 18–8 stainless steel disks fixed by gland nuts, 10, serving to hold it steady as the catalyst bed. The pressure vessel was closely wound with nichrome resistance wire in three separate sections, 11, 12, and 13, to maintain isothermal conditions in the catalyst bed. The entire length of the reactor was covered with asbestos cloth for insulation, 15. The reaction temperature was measured with chromel-alumel theremocouples, 16 and 17, inserted in 18–8 stainless steel pipes, 18 and 19. In this way the temperature of the catalyst bed was controlled within 0.25°C of the desired temperature.

Table 1. The composition of *m*-xylene used as a reactant

Benzene	Toluene	Ethylbenzene	*p*-Xylene	*m*-Xylene	*o*-Xylene
trace	trace	trace	0.2	99.6	0.2

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1) H. Takaya, N. Todo, T. Hosoya, T. Minegishi, and M. Yoneoka, This Bulletin, **43**, 2635 (1970).

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

3) K. L. Hanson and A. J. Engel, *A. I. Ch. E. Journal*, **13**, 260 (1967).

TABLE 2. COMPOSITIONS OF THE PRODUCTS WHEN POWDERED SILICA-ALUMINA WAS USED AT A PRESSURE OF 300 kg/cm^2 (wt%)

Temperature	Toluene	*p*-Xylene	*m*-Xylene	*o*-Xylene	TMB[a]	*W*/*F* g-cat·h/g
290°C	2.1	15.3	65.2	12.2	2.5	1.65
320°C	1.0	16.5	65.1	14.0	1.2	2.6×10^{-1}
380°C	0.2	12.6	76.8	10.0	t	7.0×10^{-3}
380°C	0.7	19.6	61.1	16.2	0.9	7.8×10^{-3}

a) TMB: Trimethylbenzene

In preparation for a series of runs, a weighed amount of catalyst was charged into the reactor in a dry box and moistened with *m*-xylene; then the reactor was placed in the pressure vessel. To make a run, *m*-xylene was passed through the reactor at a desired rate of 2 to 24 g/h under a pressure of 300 kg/cm^2, and then the reactor was heated to the desired temperature.

The catalyst was Nikki N633L silica-alumina crushed to a diameter of 1—1.4 mm or powdered Nikki N633L silica-alumina; both of these had been calcined at a temperature of 500°C for 20 hours. The purity of the *m*-xylene used as a reactant (produced by the Japan Gas-Chemical Co., Inc.) was 99.6 percent, as is shown in Table 1.

The product was analyzed by gas chromatography at 57°C. The column used for this measurement was 4 m in length and 1 mm in dia., and was packed with 5% bentone 34+5% DIDP on diasolid L (100—200 mesh).

In order to confirm the inhibiting effects of the high-boiling by-products on catalyst activity and to identify the components, the reaction products were fractionated under a pressure of 6—8 mm Hg and separated into several fractions. The components of the thus fractionated products were analyzed by means of a Hitachi double-beam mass spectrometer and a Varian-type NMR spectrometer. The 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.

Results and Discussion

Activity of Powdered Silica-Alumina in the Liquid-phase Reaction. A heterogeneous catalytic reaction is considered to proceed in a series of mass transfer and kinetic steps. It has already been shown, however, that, in the liquid-phase isomerization of xylene, the kinetic steps are rate-determining up to the temperature of 380°C when powdered silica-alumina is used.

The results obtained at reaction temperatures of 290°C, 320°C, and 380°C under a pressure of 300 kg/cm^2 are shown in Table 2 and Fig. 2. It has been well recognized, in a study to follow the variation in the catalyst activity, that the variation is insensitive if the reaction has been equilibrated. Therefore, in this experiments the contact times, *W*/*F* (g-cat·h/g), were lowered with an increase in the reaction temperature so as to keep the *p*- and *o*-xylene contents in the products in the region of 0.12 to 0.15. In Fig. 2, the catalyst activities for isomerization and disproportionation are represented by the contents of *p*-xylene and toluene

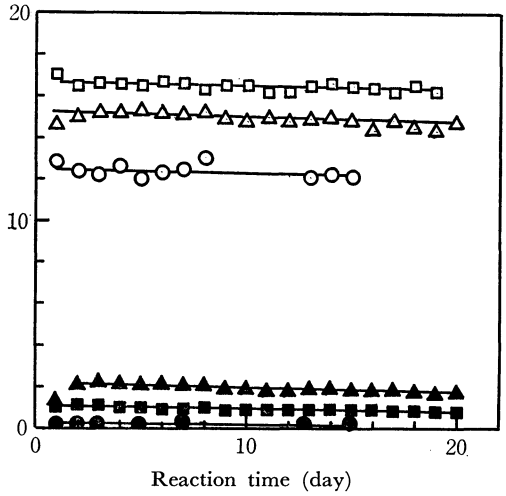

Fig. 2. Activity of powdered silica-alumina in the liquid-phase reaction at a pressure of 300 kg/cm^2.
△: *p*-Xylene, 290°C. ▲: Toluene, 290°C.
□: *p*-Xylene, 320°C. ■: Toluene, 320°C.
○: *p*-Xylene, 380°C. ●: Toluene, 380°C.

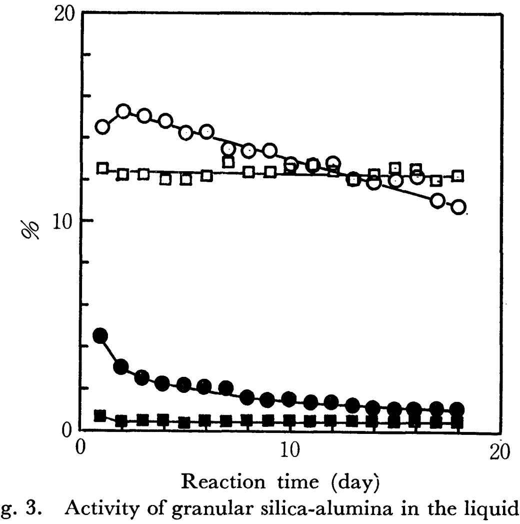

Fig. 3. Activity of granular silica-alumina in the liquid-phase reactions at a pressure of 300 kg/cm^2.
□: *p*-Xylene, 380°C. ■: Toluene, 380°C.
○: *p*-Xylene, 430°C. ●: Toluene, 430°C.

TABLE 3. COMPOSITIONS OF THE PRODUCTS OBTAINED BY USING GRANULAR SILICA-ALUMINA (1—1.4 mm in dia.) UNDER A PRESSURE OF 300 kg/cm^2. (wt%)

Temperature	Toluene	*p*-Xylene	*m*-Xylene	*o*-Xylene	TMB[a]	*W*/*F* g-cat·h/g
320°C	1.6	11.5	71.5	9.3	1.8	2.4×10^{-1}
380°C	0.5	12.2	74.9	9.9	0.5	1.5×10^{-2}
430°C	4.5	14.5	62.4	12.9	5.3	7.4×10^{-3}

respectively, since these contents are nearly equal to those of *o*-xylene and trimethylbenzene respectively. It is clear from this figure that, in each of the three cases, but not at 430°C, practically no decline in the catalyst activity for the isomerization of *m*-xylene was observed, even after 20 days.

From Table 2 it can be seen that the ratio of the toluene content to the *p*-xylene content decreased with the reaction temperature. This result is consistent with the fact that the activation energy for the disproportionation over H–Y zeolite is smaller than that for the isomerization.[4]

Activity of Granular Silica-Alumina in the Liquid-phase Reaction. In Fig. 3 and Table 3, the results obtained by using a granular silica-alumina catalyst (1—1.4 mm in dia.) are shown. Figure 3 indicates that the activity decline did not occur at the temperature of 380°C. However, at the temperature of 430°C a gradual and comparatively large decline was observed; furthermore, the initial ratio of the toluene content to the *p*-xylene content increased considerably.

In an earlier paper[2] it was shown that the ratio of toluene to *p*-xylene increased with the contact time. Therefore, the remarkable increase in the disproportionation products at a higher temperature, such as 430°C, may be partially connected with the appearance of the contribution of the diffusion step to the reaction rate. Under such reaction conditions, the high-boiling by-product may accumulate, since its diffusion rate from the pores will be slower than the accelerated rate of the formation of the high-boiling by-product. This will be the cause of the decline in activity at 430°C.

Activity of Silica-Alumina in Vapor-phase Reactions at Atmospheric Pressure. In contrast with the results obtained in the liquid-phase reaction described above, it has been reported by many workers that, in the vapor-phase reaction, a steep decline in activity is unavoidable.[3,5] In order, therefore, to get information about the characteristic difference between the reaction in the liquid phase under high pressures and that in the vapor phase at atmospheric pressure, the following measurements were carried out. The reaction was operated at 292°C under a pressure of 300 kg/cm^2; then the temperature was raised to 378°C at atmospheric pressure and kept at this temperature for 48 hr. After that, the reaction temperature was lowered again to 292°C and the pressure was increased to the initial pressure of 300 kg/cm^2. The activity indicated by the produced *p*-xylene is shown in Fig. 4. One of the most characteristic features in the vapor-phase isomerization is that the activity decreases steeply from 0.94 g/h g-cat. (B in Fig. 4) to 0.43 g/h·g-cat. (C in Fig. 4).

In addition, it must be noted that the observed activity in the vapor-phase reaction is much lower than that in the liquid-phase reaction. The vapor-phase reaction was carried out at a much higher temperature, at which a sufficient change in activity is observable, than that in the liquid phase. The comparison of the activities between the two reactions was made by the following procedure. As was reported in a preceding paper,[2] in the liquid-phase reaction under pressures the coverage of xylenes on surface sites is 1.0 and the observed activation energy for the isomerization from *m*-xylene to *o*-xylene is 37 kcal/mol, so long as the reaction temperatures are 380°C or less. Thus, the rate calculated for the isomerization from *m*- to *p*-xylene at 380°C by using this activation energy amounts to 76 times that at 292°C. On the other hand, the observed ratio of the rate for the vapor-phase reaction at 378°C to that for the liquid phase at 292°C is only 8.8. It is evident from the comparison that the activity of the silica-alumina catalyst in the liquid phase under a high pressure is much higher than that in the vapor phase.

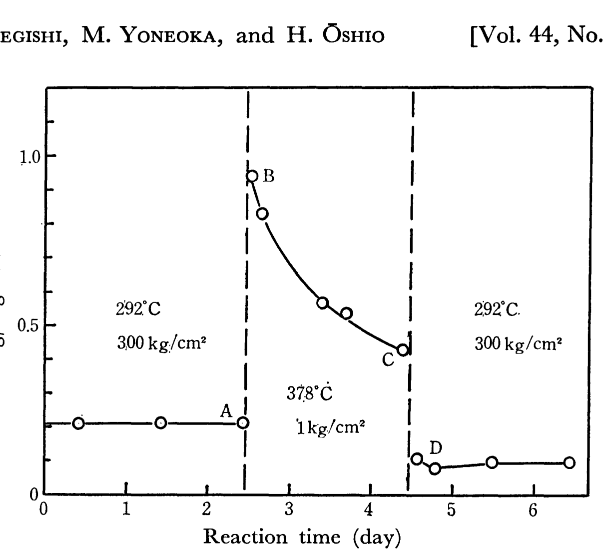

Fig. 4. Activity of silica-alumina in the vapor-phase reaction at atmospheric pressure.

Effect of the Interruption of the Flow on the Activity. As was described in the foregoing paragraph, an increase either in the contact time or in the reaction temperature tended to have the same effects on the

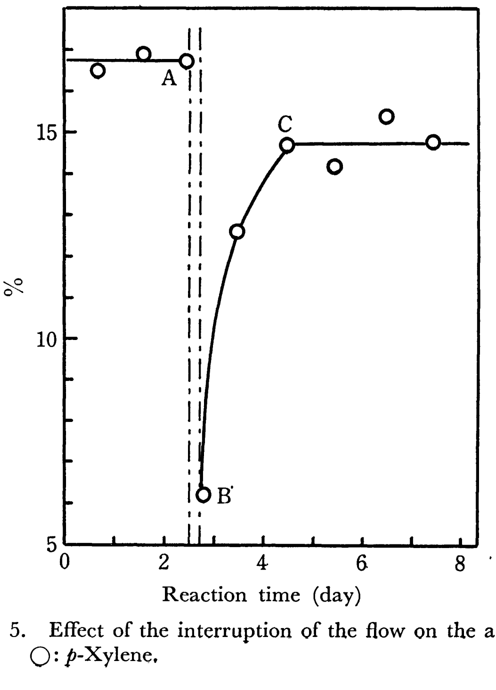

Fig. 5. Effect of the interruption of the flow on the activity. ○: *p*-Xylene.

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[4] H. Takaya, N. Todo, T. Hosoya, T. Minegishi, and M. Yoneoka, unpublished.

[5] T. Iwasaki and R. Hatta, *Kogyo Kagaku Zasshi*, **63**, 1980, (1960).

TABLE 4. THE COMPOSITIONS OF THE PRODUCTS AT THE REPRESENTATIVE POINTS IN Fig. 5 (Wt%)

Sample[a)]	Toluene	*p*-Xylene	*m*-Xylene	*o*-Xylene	TMB	TeMB[b)]	X[c)]
A	0.8	16.6	65.2	14.1	0.9		2.4
B_1	6.6	7.3	56.1	6.2	8.7	1.1	14.0
B_2	0.4	6.6	83.3	4.9			4.8
C	0.6	14.7	69.0	12.0	0.8		2.9

a) A: before the interruption of the flow. B_1 and B_2: 1.5 and 2.5 hr respectively after the resumption of the flow. C: 2 days after the resumption of the flow.

b) TeMB: Tetramethylbenzene.

c) X: Unidentified products.

product distribution and on the activity of the catalyst. In order, therefore, to get more detailed information about the effect of the product distribution on the decline in the activity, as an extreme case the flow of the feed was interrupted for 5 hr in the course of a stationary reaction at 320°C under 300 kg/cm^2; the consequent variations in the activity and in the product distribution were followed. As is shown in Fig. 5, the *p*-xylene content decreased from a value of 16.6% before the interruption of the flow (A in Fig. 5) to 6.6% immediately after the resumption of the flow (B_2 in Fig. 5), and was then restored to an incomplete level of 14.7% after a two-day reaction. The compositions of the products at the representative points shown in Fig. 5 are tabulated in Table 4. From a comparison of the composition at 1.5 hr after the resumption of the flow (B_1) with those at A and C, it can be seen that the interruption of the flow results in an extraordinary increase in the disproportionation products and unidentified high-boiling by-products. On the basis of these results, it can be considered that the unidentified products, X, presumed to be responsible for retarding the isomerization, were accumulated on the surface sites of the catalyst during the interruption of the flow and were then eluted into the reactant solution after the resumption of the flow.

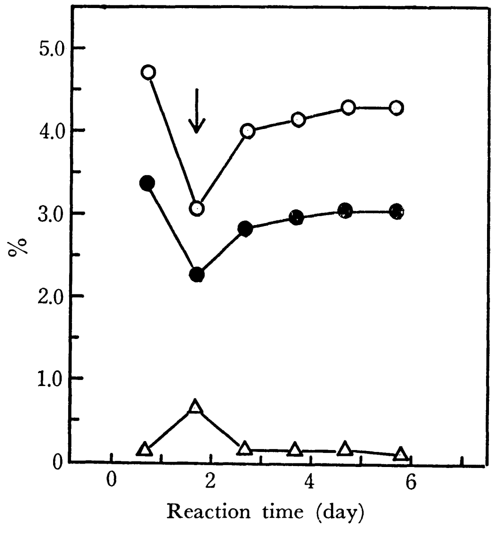

Fig. 6. Effect of the fraction 2 on the activity.
A downward arrow shows that a *m*-xylene solution containing 2 weight per cent fraction 2 was passed through the catalyst bed for 4 hr.
Reaction temperature: 280°C.
○: *p*-Xylene. ●: *o*-Xylene. △: Toluene.

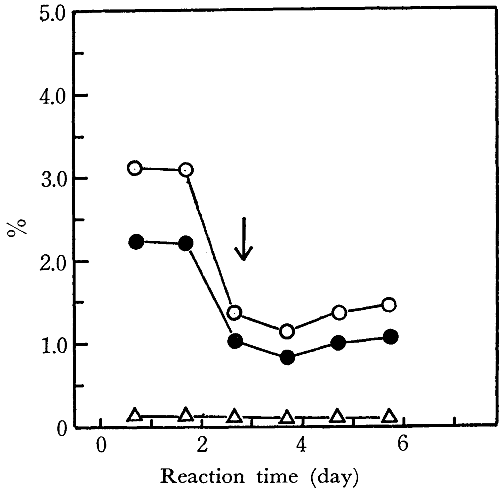

Fig. 7. Effect of the residue on the activity.
A downward arrow shows that a *m*-xylene solution containing 1 weight per cent residue was passed through the catalyst bed for 4 hr.
Reaction temperature: 280°C.
○: *p*-Xylene. ●: *o*-Xylene. △: Toluene.

The Effect of High-boiling By-products on the Activity. An experiment was carried out at 400°C under a pressure of 300 kg/cm^2, where the high boiling by-products could be produced in high yields. The total product after 9 days' operation, 1000 g, was distilled under a reduced pressure of 6—8 mmHg in the temperature ranges of 100—125°C (fraction 1), 125—150°C (fraction 2), and 150—200°C (fraction 3). The yields of these fractions and the residue are shown in Table 5.

Figures 6 and 7 show, respectively, the effects of the addition of fraction 2 and the residue on the activities; *m*-xylene solutions containing 2 weight percent of fraction 2 and 1 weight percent of the residue were passed through the catalyst bed for 4 hr in the course of a stationary reaction, using pure *m*-xylene as the reactant at 280°C under a pressure of 300 kg/cm^2. From Fig. 6 it is obvious that, by the addition of a minute quantity of the fraction 2, the *p*-xylene and *o*-xylene contents diminished and the toluene content increased. The varied contents were, however, restored to levels of about 90 percent of the initial values 4 days after the reactant was changed to pure *m*-xylene. As to the experiment with using a *m*-xylene solution containing 1 weight percent of the residue, the effect differed from that of fraction 2, as is shown in Fig. 7, the contents of *p*-xylene and *o*-xylene diminished to values less than half of the initial contents, whereas

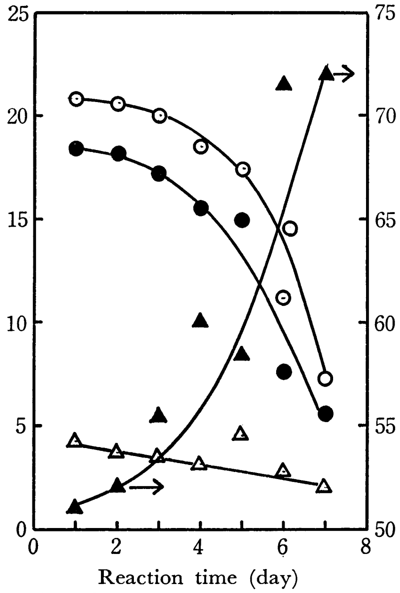

Fig. 8. Activity of silica-alumina at atmospheric pressure. W/F=0.5 h.

	1st day	2nd	3rd	4th	5th	6—7th
Reaction temperature(°C)	430	440	450	460	490	500

○: p-Xylene. ●: o-Xylene. ▲: m-Xylene. △: Toluene.

the toluene content was unaltered. Moreover, in this case, the reduced contents of p- and o-xylene were scarcely restored even 4 days after the reactant had been changed to pure m-xylene. The results clearly indicate that the high-boiling by-products have an inhibiting effect on the isomerization of m-xylene.

In contrast to the case of the liquid-phase isomerization under high pressure, only 1 g of high-boiling by-products could be separated from the product (800 g) obtained by 7 days reaction operated at a temperature above 430°C under atmospheric pressure. This result, when considered in connection with the remarkable decline in activity shown in Fig. 8, indicates that, in the vapor-phase isomerization high-boiling by-products are not easily desorbed from the catalyst surface, but are accumulated on the surface, this accumulation results in a large decline in the activity and in the low activity in the vapor-phase reaction.

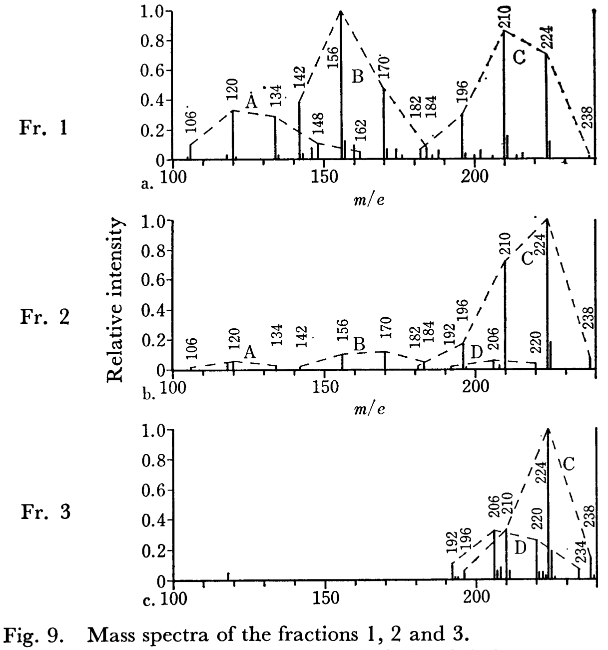

Fig. 9. Mass spectra of the fractions 1, 2 and 3.
A: Polymethylbenzene. B: Polymethylnaphthalene.
C: Polymethyldiphenylmethane. D: Polymethylanthracene or Polymethylphenanthrene.

Identification of High-boiling By-products. Figure 9 shows the mass spectra of the fractions 1, 2, and 3. It can be seen that all the spectra consist of several homologous series of the parent peaks: the successive peaks in a homologous series differ in mass number by 14, corresponding to the replacement of a hydrogen atom by a methyl group.

In the fractions 1 and 2, three series of polymethyl compounds were observed: A and B correspond to polymethylbenzene and polymethylnaphthalene respectively, while C corresponds to polymethyldiphenyl, polymethyldiphenylmethane, or polymethyldiphenylethane. The D series in the fractions 2 and 3 was identified as polymethylanthracene or polymethylphenanthrene.

Table 5. High-boiling by-products separated from the products (1000 g) of the reaction at 400°C under a pressure of 300 kg/cm². Distillation pressure: 6–8 mmHg

Fraction number	Temperature range (°C)	Yield (g)
1	100—125	3.2
2	125—150	14.7
3	150—200	3.0
Residue		1.4

As is shown in Table 5, the yield of fraction 2 amounts to 70 percent of total high-boiling by-products.

Therefore, the studies were concentrated upon the more accurate identification of the possible components of the main series, C. For this purpose, the fraction 2 was analyzed by means of NMR spectroscopy. The observed spectrum shows that all the polymethyl compounds have a methylene group in their structures. Moreover, the ratio of the number of the hydrogen atom in the methyl group to that in the methylene group was 6.5, and the ratio of the number of the hydrogen atom bound to the aromatic ring to that in the methylene group was 4.0. These findings imply

Table 6. Ratios of numbers of hydrogen atoms in the methyl group and bound with aromatic rings to that in methylene groups

	$-CH_2-$	$-CH_3-$	$-H$
The observed ratio for the fraction 2	1	6.5	4

The calculated ratios from the formulas

Mass number	Polymethyl-diphenylmethane			Polymethyl-diphenylethane		
	$-CH_2-$	$-CH_3$	$-H$	$-CH_2-$	$-CH_3$	$-H$
196	1	3	4	1	0.75	2.25
210	1	4.5	3.5	1	1.5	2
224	1	6	3	1	2.25	1.75

that the existence of polymethyldiphenyl should be excluded. Thus, the component must be either polymethyldiphenylmethane or polymethyldiphenlethane. The ratios calculated from the formulas of these compounds are also shown in Table 6. The agreement between the calculated and observed values is not satisfactory. However, it seems to be reasonable to say that the main component in the C series is polymethyldiphenylmethane rather than polymethyldiphenylethane, when one takes into account the fact that minute amounts of the compounds which have no methylene group, such as polymethylnaphthalene and polymethylanthracene, raise both the ratios.

We are very grateful to Dr. Yamamoto for his help in the measurements of the NMR spectra and to Dr. Fukuda for his help in the measurements of the mass spectra.