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Dehydrocyclization of 3-Methyl Heptatriene-1, 4, 6

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Xylenes, mainly consisting of *p*-xylene and *o*-xylene, were selectively synthesized by the dehydrocyclization of 3-methyl heptatriene-1, 4, 6 (MHT) using a chromia-alumina catalyst. MHT was easily converted to xylenes in a good yield; this reaction proceeded even under mild conditions, as at 200°C. The effects of the catalyst composition, and the influence of the reaction temperature on the conversion of MHT, the xylene yield, the by-products, *etc.*, were studied.

The dehydrocyclization of 3-methyl heptatriene-1, 4, 6 (MHT), obtained by butadiene oligomerization,[1-4] was carried out using chromia-alumina, molybdena-alumina, and platforming catalysts.

Though many reports[5-13] have been presented regarding the dehydrocyclization of paraffins

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and olefins, and investigating the catalyst, the mechanism of dehydrocyclization, *etc.*, the dehydrocyclization of trienes such as MHT has not yet been examined. It was found that MHT was converted to xylenes (including ethylbenzene) in a good yield with a trace of *m*-xylene.

Experimental

MHT. MHT was obtained through the oligomerization[2] of butadiene by a cobalt(III) acetylacetonate-triethyl aluminum catalyst. Bp 57—58°C/100 mmHg; purity, 98.6%.

Catalyst. All the catalysts except the platforming catalyst were prepared by the impregnation method; active alumina (8—14 mesh) was used as the support, and an aqueous solution of metal nitrates was used as the catalyst-metal source. Each catalyst was pretreated with oxygen at 500—550°C for 2 hr. The platforming R-7 catalyst was used as the platinum alumina catalyst.

Apparatus and Procedure. A conventional flow-type reactor was used as the experimental apparatus. After 50 cc of catalyst had been placed in it, the reactor (d. 15 mm, l. 100 cm) was kept at 500°C for 2 hr in a hydrogen stream; the reaction of MHT (LHSV 1.0—1.3 v/v/hr) was carried out at the reaction temperature and at a normal pressure of the hydrogene stream (H_2/MHT mol ratio 1.0—1.3). Beginning 5 min after the first drop of the product appeared, liquid and gas were collected during a 1-hr period as the reaction products. The liquid product was analyzed by gas chromatography (PEG column; d. 0.15 mm, l. 90 m, 90°C) and the gas was analyzed both by gas chromatography and using a mass spectrometer (Hitachi RMU-5). A typical gas chromatogram of the reaction product is shown in Fig. 4.

Results

Catalyst. Several kinds of catalysts were examined in order to compare the catalyst activity and the selectivity in the dehydrocyclization of MHT. The results are shown in Table 1. It was found that, except for the platforming catalyst, the catalysts used produced a xylene fraction which contained only a trace of *m*-xylene, and that the total aromatics yield decreased in the following order: chromia-alumina, molybdena-alumina, and the platforming catalyst. Under these experimental conditions, the K_2O-Ce_2O_3-Cr_2O_3-Al_2O_3 catalyst showed the best xylene yield, but even in the other catalysts, xylenes were obtained in 52—82 wt% yields per pass. It is very interesting that *m*-xylene were not formed when the chromia-alumina or molybdena-alumina catalysts were used, but when the platforming catalyst was used, *m*-xylene was formed at nearly the same level of equilibrium content.

Influence of Temperature. In the case of the chromia-alumina catalyst, the reaction conditions, the xylene yield, the by-products, *etc.* were investigated.

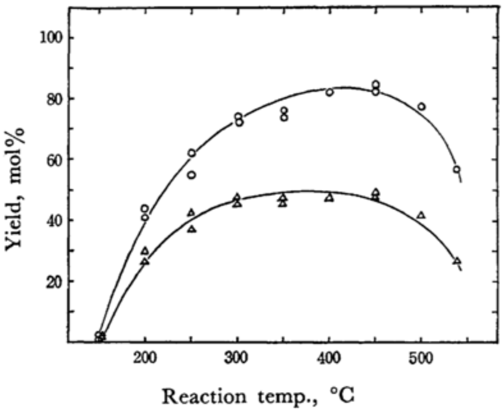

Fig. 1. Relation between xylenes yield and reaction temperature with K_2O-Ce_2O_3-Cr_2O_3-Al_2O_3 catalyst.

—○— Total xylenes —△— *p*-Xylene

1) MHT Conversion and Xylene Yield. In the experimental reaction temperature range (150—540°C), the conversion of MHT reached 99—100 mol% (Fig. 1). In the case of the dehydrocyclization of *n*-heptane[8] and 3-methyl heptane[9], the conversion was 41.7% (*n*-heptane) under the same conditions as those used for MHT, and 31—41% (3-methyl heptane) at the temperature of 527°C and the contact time of 3 sec using a chromina-alumina catalyst. When these data were compared with those of MHT, it was considered that the conversion rate of MHT was faster than that of paraffins and olefins. At reaction temperatures higher than 200°C, the higher the temperature, the better the yield of xylenes. At 400—450°C the xylene yield reached maximum; at temperatures higher than 450°C much decomposition and coking began to occure, causing a decrease in the yield of xylenes. The maximum yield of xylenes was attained at the reaction temperature of 450°C, and the total yield of xylenes and *p*-xylene were 82.0 wt% and 48.4 wt% respectively. Akiyoshi and his co-workers[10] obtained a maximum aromatics yield of 53.0% in the dehydrocyclization of 3-methyl heptane with the chromia-alumina catalyst at 450—570°C, and Pines[9] reported that the xylene yield was 10—20 wt% in the aromatization of 3-methyl heptane with the chromia-alumina catalyst.

In comparing these results, it should be noted that MHT has a higher reactivity than paraffinic hydrocarbons with the same carbon skeltone.

2) Xylene Composition. As shown in Fig. 2, the *p*-xylene content in the xylenes decreased slowly, while the *o*-xylene and ethylbenzene contents gradually increased with the temperature increase. It is remarkable that no *m*-xylene was found below 400°C, while at 400°C a trace of *m*-xylene appeared and at higher temperatures, *m*-xylene was formed in small amounts.

3) By-products. Many kinds of by-products, but in small amounts found in the products. Benzene

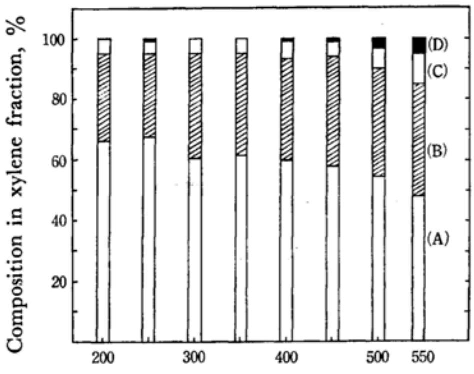

Fig. 2. Xylene composition at various reaction temperature.
(A) *p*-Xylene (B) *o*-Xylene
(C) Ethylbenzene (D) *m*-Xylene

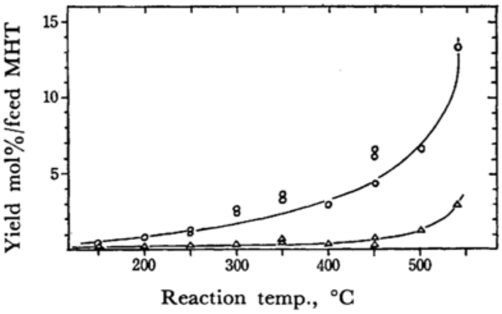

Fig. 3. Benzene and toluene yield.
—○— Toluene —△— Benzene

and toluene were produced in small amounts, but their yields showed a rapid increase above 500°C (Fig. 3)

In our discussion, the other by-products were classified into 2 groups, unknown group 1 (UK-1) and unknown group 2 (UK-2). The UK-1 group has a shorter retention time than toluene in the gas chromatogram (PEG Golay type column, 90°C), while the other has a longer one, as shown in Fig. 4. The boiling points of these unknown substances were determined by means of squalane column gas chromatography (Golay type, 90°C), caliburated by standard hydrocarbon smaples. UK-1 consisted of 9 main compounds; the boiling range assumed to be 85—111°C. UK-2 had 5 major compounds and a boiling range assumed to be 111—135°C. The relationship between the unknown-substance yields and the reaction temperature is shown in Fig. 5. A distinct difference in temperature dependency appeared between the amounts of UK-1 and of UK-2. The UK-1 yield almost does not change at all over the experimental-reaction temperature range. On the con-

TABLE 1. DEHYDROCYCLIZATION OF MHT WITH VARIOUS CATALYSTS

Exp. No.	X-2	X-4	X-7	X-8	X-151
Catalyst					
Components	K_2O	Cr_2O_3	MoO_3	MoO_3	Pt
	Ce_2O_3	Al_2O_3	Al_2O_3	Al_2O_3	
	Cr_2O_3				
	Al_2O_3				Al_2O_3
Composition (wt%)	1.7	12.1	12.1	12.1	0.36
	1.5	87.9	87.9	87.9	
	12.1				
	84.7				98.9
Reaction temp. (°C)	450	450	450	400	450
MHT conversion (mol%)	99.9	99.9	99.9	99.9	99.5
Yield of					
Liq. products (wt%)	94.3	95.5	95.3	95.2	81.2
Aromatics (mol%)	84.1	86.1	80.8	68.3	57.2
Xylenes (mol%)	83.8	82.6	75.7	64.1	52.7
Comosition of liq. product (wt%)					
Benzene	0.7	0.3	0.5	0.6	0.5
Toluene	7.4	6.1	7.4	6.5	4.1
Ethylbenzene	4.4	6.6	7.5	6.0	3.8
m-Xylene	0.4	0.3	0.9	0.9	21.4
p-Xylene	49.2	46.4	40.5	34.9	25.1
o-Xylene	29.4	28.9	26.4	22.1	13.4
MHT	0.1	0.1	0.1	0.2	0.6
UK-1	7.5	10.7	16.2	27.6	20.5
UK-2	0.7	0.6	0.2	1.0	3.2
C_8 up	tr	tr	0.3	0.2	7.4

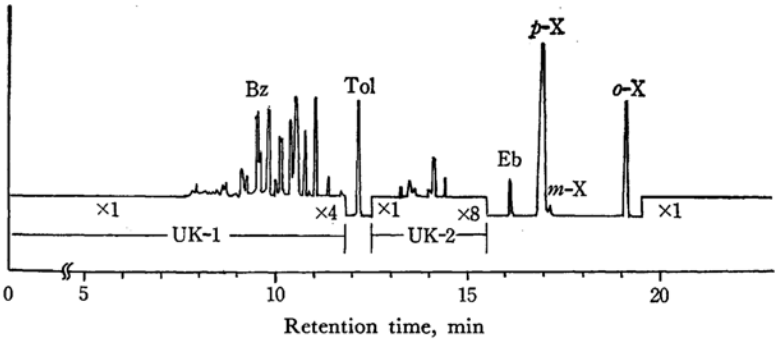

Fig. 4. Reaction product gas chromatogram.

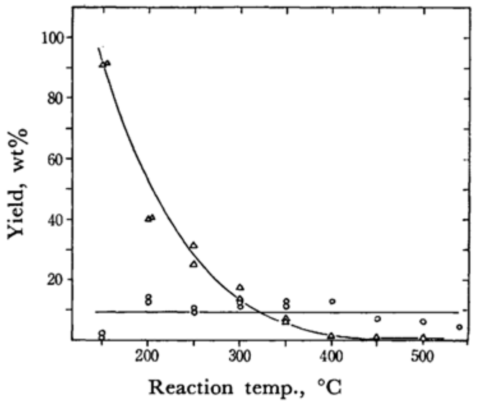

Fig. 5. UK-1 and UK-2 Yield.
—○— UK-1 —△— UK-2

trary, UK-2 was not detected above 400°C, and the UK-2 yield decreased along with the temperature increase, until at 150°C the yield reached about 90%. This reaction product, containing about 90% UK-2, was used instead of MHT as a reaction feed stock for the dehydrocyclization in order to ascertain the character of UK-2. The reaction of this feed stock, diluted with benzene, was carried out at 450°C using a K_2O-Ce_2O_3-Cr_2O_3-Al_2O_3 catalyst. The products of this reaction were analyzed, and the xylene yield calculated. It was found that, the xylene composition and yield were about the same as when MHT was used as the feed stock (Table 2).

4) Deposit on the Catalyst. The yields of the substances on the catalyst at 150—540°C are shown in Fig. 6. It is very interesting to see that deposit-material yield showed a minimum at 300°C. At 500°C, after the reaction, the catalyst surface was covered with a black material which looked like carbonaceous matter, but at 150°C and 200°C, the appearance of the catalyst did not change after the reaction. The reason for the different appearances between 150°C and 540°C was clarified by carbon and hydrogen analyses of these spent catalyst. At 150°C, 200°C, and 540°C the C/H ratios were 6.4, 6.5, and 19.2 respectively (8.0 in MHT). These results shown that, at higher

TABLE 2. DEHYDROCYCLIZATION OF UK-2

Exp. No.	X-141
Catalyst	K_2O-Ce_2O_3-Cr_2O_3-Al_2O_3[*1]
Reaction temp. (°C)	450
Feed composition (wt%)	
UK-1	1.6
UK-2	58.5
Benzene	39.9
Yield of (mol%)	
Benzene	−2.0[*2]
Toluene	2.4
Ethylbenzene	4.0
p-Xylene	39.0
m-Xylene	0.0
o-Xylene	19.5
UK-1	18.6
UK-2	2.1
C_8 up	0.3
Xylenes	62.6
Aromatics	62.9

[*1] Composition was same as exp. No. X-2 (Table 1).

[*2] Charged benzene (for diluent) was not completly recovered, and so the yield showed minus value.

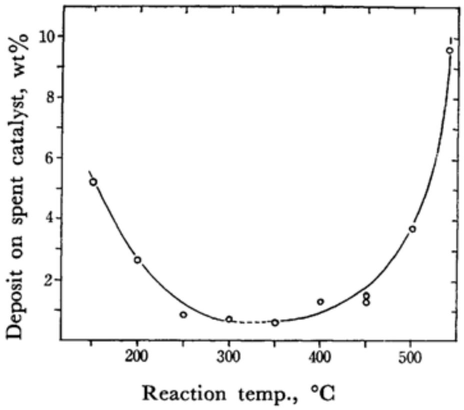

Fig. 6. Deposit on spent catalyst at various reaction temperatures.

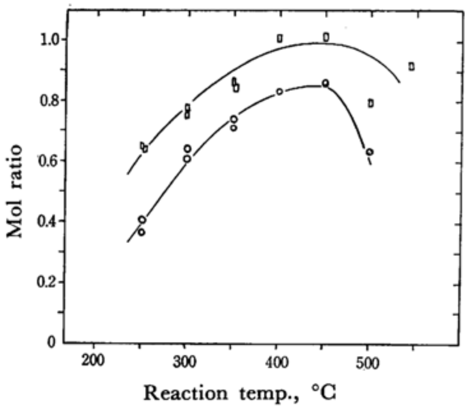

Fig. 7. Evolved hydrogen yield.
—□— H_2/Formed xylenes
—○— H_2/Consmed MHT

temperatures, the deposits on the catalyst were mainly coke, whereas at lower temperatures they seemed to be polymerization products of MHT.

5) Exit Gas. All the exit gas except that at 540°C consisted of 99—90% hydrogen. The mole ratios of evolved hydrogen/consumed MHT and evolved hydrogen/formed xylenes at 200—540°C are shown in Fig. 7. At the reaction temperature between 300—450°C, hydrogen was evolved about stoichiometrically to the xylenes formed, and the evolved hydrogen/consumed MHT mole ratio was about 0.8, which was helpful in estimating the reaction mechanism.

Discussion

Without a catalyst, only 2.5% and 8% of the MHT was converted, the rest was recovered as MHT at 300°C and 450°C respectively. This shows that thermal reaction can be neglected, and that the xylene-formation reaction is undoubtedly accelerated by these catalysts.

On the basis of the above results, let us suggest an alternative assumption regarding the route by which MHT is converted to aromatics:

(1) At first the cyclization of MHT takes place, followed by dehydrogenation.

(2) On the contrary, the dehydrogenation of MHT took place first, and then cyclization took place.

It was presumed, except in the case of the platforming catalyst, that this reaction was carried out *via* the route of assumption (1); this presumption is based on the fact that the amount of hydrogen evolved was about stoichimetrical to the xylenes. Though many dehydrocyclization mechanisms have been presented and discussed,$^{9-13)}$ *m*-xylene was not formed from MHT; therefore, it seemed in the case of MHT that neither isomerization in its carbon skelton$^{13)}$ nor the formation of a severn-membered ring took place$^{9)}$ during this reaction.

Table 3. Reaction of xylenes on chromia-alumina and platforming catalyst

Exp. No.	X-111	X-112
Catalyst	Plat. R-7*	K_2O-Ce_2O_3-Cr_2O_3-Al_2O_3**
Reaction temp. (°C)	450	450
LHSV (v/v/hr)	1.24	1.19
H_2/Feed mole ratio	0.963	0.963
Feed composition		
p-Xylene	62.3	62.0
o-Xylene	36.0	36.8
m-Xylene	0.7	0.0
Ethylbenzene	0.2	0.3
Product composition		
p-Xylene	61.3	62.0
o-Xylene	36.3	36.8
m-Xylene	1.5	0.0
Ethylbenzene	0.3	0.2
Benzene	0.1	tr
Toluene	0.4	0.1

* Composition was same as exp. No. X-151 (Table 1).
** Composition was same as exp. No. X-2 (Table 1).

In our experiments we could not ascertain what kind of intermediate was formed, but xylenes were formed from UK-2 as they were from MHT, and the fact that the catalyst deposit was about the same C-H ratio as that of MHT is very helpful in finding the intermediate.

In the case of the platforming catalyst, the products contained a lot of *m*-xylene. A mixture of *o*- and *p*-xylene was treated at 450°C with the platforming and K_2O-Ce_2O_3-Cr_2O_3-Al_2O_3 catalysts in order to ascertain the difference in these catalysts effects (Table 3). The resulting product composition was the same within the limit of experimental error; this showed that the platforming catalyst did not isomerize *o*- and *p*-xylene. Therefore, it could be understood that the *m*-xylene in the product was not the isomerization product of the *o*- and *p*-xylene which came from the dehydrocyclization of MHT. According to this finding, it could be estimated that, on the platforming catalyst, the dehydrocyclization mechanism of MHT was different from the cases of the chromia and molybdena catalyst.

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