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Dehydrocyclization of Paraffins. Influence of Chlorine on Cyclization Pathway over Pt–Al_2O_3 Catalysts

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Platinum–alumina catalysts are usually prepared by impregnation with chloroplatinic acid (*1*). McHenry *et al.* (*2*), have proposed that a fraction of the chloroplatinum complex survived the catalyst pretreatment; this complex—but not metallic platinum—was soluble in aqueous HF. They found that dehydrocyclization was catalyzed only by the soluble chloroplatinum fraction; isomerization and cracking were catalyzed by the metallic platinum. Other laboratories subsequently reported results which supported this proposal (*3–5*). Bursian *et al.* (*6*) claimed that the soluble Pt–Cl–Al_2O_3 complex was even more specific and catalyzed only cyclizations to naphthenes and that all dehydrogenation took place on the metallic platinum. In contrast, Kluksdahl and Houston (*7*) and Johnson and Keith (*8*) found that the soluble platinum was present only after the reduced catalyst was exposed to oxygen. Thus, the soluble form could not be the active dehydrocyclization catalyst but may still be the source of the Pt active for dehydrocyclization.

The aromatic isomer distribution may be influenced by the various catalytic materials (*9*); hence, it could be expected that a different isomer distribution may be obtained when chlorine is present than when it has been removed. Thus, we have determined the aromatic isomer distribution for the dehydrocyclization of 3-methylheptane over catalysts with and without chlorine.

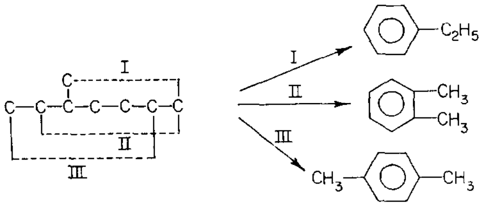
EXPERIMENTAL METHODS

The catalysts were prepared by impregnation of "nonacidic" alumina with chloroplatinic acid. The chlorine was removed from a portion of the reduced catalyst by ammonium hydroxide (*10*). A Pt–SiO_2 catalyst was prepared by the same procedure; however, the material continued less than 0.01% chlorine after reduction at 550°C.

The dehydrocyclization was accomplished in a flow apparatus (*10*). Experimental conditions were: 482°C, atmospheric pressure, and 0.3 LHSV. C_8-Aromatics were analyzed by GLC using a Bentone 34/diisodecyl phthalate column.

RESULTS AND DISCUSSION

We presented evidence (*10*) that the major aromatic isomer products from dehydrocyclization over Pt–Al_2O_3–K were those predicted by a direct cyclization to a six-carbon ring structure. For 3-methylheptane, three such cyclization pathways are possible:



Equal amounts of the above isomers have been predicted for direct cyclization to six-carbon cyclics (*11*). However, this rule will probably be unable to account quantitatively for the distribution since the catalyst influences the distribution (*9*).

The results for dehydrocyclization using two chlorine-containing Pt–Al_2O_3 catalysts, a "chlorine free" Pt–Al_2O_3 catalyst, and a Pt–SiO_2 catalyst are presented in Table 1.

TABLE 1

C_8-AROMATIC DISTRIBUTION FOR THE DEHYDROCYCLIZATION OF 3-METHYLHEPTANE AT 482°C

Catalyst	Sample	Time on stream (min)	Liquid collected (ml)	Conv to aromatic[a]	C_8-Aromatic products (mole %)			
					Ethylbenzene	Xylene isomers		
						p	*m*	*o*
$Pt–Al_2O_3–K$, 0.6%	1	33	0.4	21	22	47	4.3	27
	2	71	1.0	14	20	48	3.9	27
	3	102	1.0	10	19	52	<1.0	29
$Pt–Cl–Al_2O_3–K$, 0.6%	1	39	0.4	22	15	42	19	24
	2	76	1.0	12	16	45	16	23
	3	117	1.0	6	16	45	16	23
1.7%	1	40	0.4	22	17	38	22	22
	2	50	1.0	12	16	39	24	22
	3	130	1.3	6	18	35	25	22
$Pt–SiO_2$, 0.6%	1	36	0.6	14	19	48	4.2	28
	2	83	1.4	6	16	51	5.0	28

[a] The conversion to aromatic is given for reference only; the conversion is based on liquid products collected and does not take into account the small, variable amount of cracking with the different catalysts.

m-Xylene, the unpredicted isomer, is present in all the runs; the amount formed increases as the chlorine–platinum content increases (the wt % Pt = wt % Cl for the unwashed catalysts; this would correspond to $Pt–Cl_6$). More of the *m*-xylene was formed with the 1.7% $Pt–Cl–Al_2O_3$ catalyst than two of the three predicted isomers, *o*-xylene and ethylbenzene. Thus, the distribution of the four isomers formed over the chlorine-containing catalysts appears to differ from the $Pt–Al_2O_3–K$ and $Pt–SiO_2$ catalyst.

m-Xylene is the only C_8-aromatic allowed by direct six-carbon ring formation for both 2- and 4-methylheptane. Both of these methylheptane isomers could be formed from 3-methylheptane by a simple 1,2-methyl migration. The data in Table 2 was calculated assuming that *m*-xylene was formed from 2- and 4-methylheptane and should be excluded when calculating the isomer distribution. A comparison of the data in Table 2 led us to conclude that the same C_8-aromatic isomer distribution is obtained over catalysts with and without chlorine.

TABLE 2

C_8-AROMATIC ISOMER DISTRIBUTION CALCULATED BY DISREGARDING *m*-XYLENE[a]

Catalyst	Ethylbenzene	*o*-Xylene	*p*-Xylene
$Pt–Al_2O_3–K$	23	28	49
$Pt–Cl–Al_2O_3–K$, 1.7%	22	29	49
0.6%	18	30	52
$Pt–SiO_2$	20	31	50

[a] For first sample for each run.

We conclude that the presence of chlorine does not alter the selectivity, and hence reaction pathway, for the dehydrocyclization of paraffins. The chlorine provides an easier methyl migration pathway than a catalyst without chlorine. Since 0.8 wt % Cl, added to $Pt–Al_2O_3–K$ as NH_4Cl, did not have nearly as much effect on the isomer distribution as 0.6% Cl in the 0.6% $Pt–Cl–Al_2O_3$, the chlorine added as chloroplatinic acid is probably a specific type.

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