The Hydrocracking of a Heavy Anthracene Oil over Molten Salt Catalysts[1)]

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The hydrocracking of a heavy anthracene oil over molten salt catalysts (zinc chloride or a binary mixture of zinc chloride and another metal chloride) at 400 °C for 3 h in a batch autoclave system was carried out, and the products were mainly identified by means of GC-MS. The effects of the hydrogen pressure (60 or 100 kg/cm^2), the quantity of the catalyst, and the addition of metal chloride (potassium chloride or copper(I) chloride) to zinc chloride on the product distribution were examined and discussed. Based on the detailed product analysis, it was found that *cata*-condensed polycyclic aromatic compounds were hydrocracked more efficiently than *peri*-condensed polycyclic aromatic compounds. The $CuCl/ZnCl_2$ molten salt displayed an excellent catalytic activity for the hydrocracking of the heavy anthracene oil.

The ring structures of the constituent units of bituminous coals are highly aromatic, and the average-sized configuration is considered to be three or four rings.[2,3)] In order to obtain a high yield of gasoline from coal, it is necessary to hydrocrack the constituent units to benzene and its derivatives. From this point of view, the hydrocracking of model compounds, which are supposed to be constituent units of coal, has been investigated.[3–12)] Zielke *et al.*[5)] had shown molten zinc chloride to be a superior catalyst for the hydrocracking of pyrene and coal extracts when used in high concentrations. Incidentally, intensive investigations have been under way in our laboratory on the catalytic action of molten salts in several organic reactions.[13)] As a part of this study, this paper will describe the hydrocracking of a heavy anthracene oil, which thus seems to be a kind of model substance. In addition, the change in the hydrocracking activity of zinc chloride by the addition of another metal chloride will be shown in this investigation.

Experimental

The NMR spectra were recorded by means of a JEOL JNM-PS-100 spectrometer, using tetramethylsilane as the internal standard. The GLC analyses were performed on a Shimadzu GC-3AH for gaseous products and on a GC-4BPTF for liquid and solid products. The GC-MS spectra were taken with a Hitachi RMU-6MG spectrometer at 20 eV connected with a Hitachi M 5201 apparatus using a 3 m × 3 mm column of 5% Silicone OV-1 on Uniport KS. The zinc chloride and potassium chloride were obtained from Wako Pure Chemical Industries, Ltd. The copper(I) chloride was obtained from Nakarai Chemicals, Ltd.

Characterization of Feed. A heavy anthracene oil (obtained from Osaka Gas Co., Ltd.; Specific gravity (50/4 °C) 1.142; moisture 0.5%; distillation test (dehydrated sample) 0—360 °C: 28.0%) was separated into three fractions and a residue by means of vacuum distillation. The characterization of these fractions is shown in Tables 1 and 2. Small amounts of heteroaromatics (indole, quinoline, carbazole, benzocarbazoles, and dibenzothiophene) were found in the feed and were identified using GC-MS. The type-analyses undertaken according to the Speight method[14)] (Table 3) gave results in good agreement with the results based on the information obtained from GC-MS.

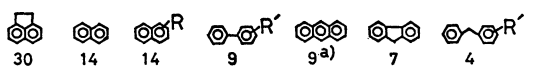
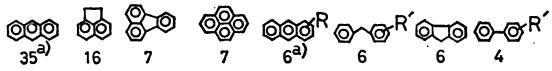
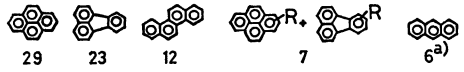
TABLE 1. CHARACTERIZATION OF FEED

Fraction No.	Distillation conditions (°C/mmHg)	M.W.	Elemental analysis (wt%) C	H	N	S	O[a)]
I	—130/10	147	92.18	6.57	0.59	—	0.66
II	120—170/5	182	92.29	5.68	0.92	0.19	0.92
III	120—190/10^{-3}	203	92.21	4.86	1.07	0.25	1.61
IV	the residue	242	92.07	4.88	1.45	0.31	1.29

a) Difference

General Procedure. All the experiments were carried out in a stainless steel (Sus 32) autoclave with a capacity of 500 ml, shaken in a horizontal direction (70 strokes/min). A stainless steel vessel containing feed (about 20 g) and the catalyst were placed in the autoclave. The air in the autoclave was replaced by hydrogen, and then the system was filled with hydrogen to the determined pressure. The rate of the temperature rise was controlled to about 3 °C/min to 400 °C. The temperature was then held at the desired level for 3 h. After the system had been cooled to room temperature, gases were admitted into a gas holder and analyzed by GLC (60—80 mesh Silica gel column 3 m × 3 mm). Solid samples from the reaction products were dissolved in a proper solvent and analyzed by GLC (4.5 m × 3 mm column packed with 20% SE-30 on Uniport B 60—80 mesh). The liquid products were also analyzed by GLC. The mixture of coke and catalyst obtained after the extraction of the products was washed with water and refluxed in hydrochloric acid to remove the catalyst. The hydrogen sulfide evolved was trapped by the use of an iodine solution, and its quantity was determined by titrating the resulting solution with a sodium

TABLE 2. MAIN COMPONENTS IN FEED IDENTIFIED BY MEANS OF GC-MS

Fraction No.	Main component (wt%)
I	 30 14 14 9 9[a)] 7 4
II	 35[a)] 16 7 7 6[a)] 6 6 4
III	 29 23 12 7 6[a)]
IV	Benzopyrenes 56  29 R = Me, Et R′ = H, Me

a) Containing phenanthrene-type compounds.

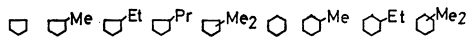
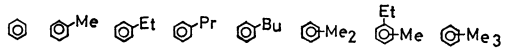
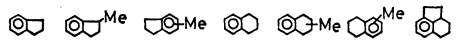
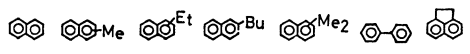
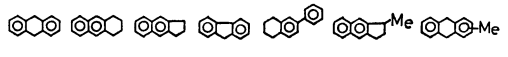
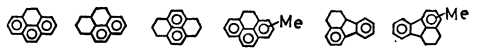
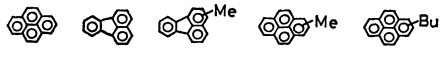
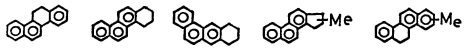
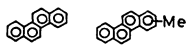
Table 3. Type analysis by the Speight method

Fraction No.	Cs/Csα	Csα/Cp	Cp/Ca	Ra
I	1.2	0.17	0.79	2.0
II	1.1	0.10	0.70	2.9
III	1.1	0.07	0.61	3.9
IV	1.2	0.06	0.61	4.5

thiosulfate solution.

Analysis of Products. The products were mainly identified by using GC-MS; in order to characterize the activities of the molten salt catalysts, they were conveniently classified into fourteen groups as follows; **1**, C_1—C_4 gases; **2**, C_5—C_7 alkanes; **3**, cycloalkanes; **4**, monocyclic aromatics; **5**, indans and tetralins; **6**, bicyclic aromatics; **7**, partially hydrogenated compounds of tricyclic aromatics, fluorenes and benzindans; **8**, tricyclic aromatics; **9**, partially hydrogenated compounds of pyrenes and fluoranthenes; **10**, pyrenes and fluoranthenes; **11**, hydrochrysenes and its isomers; **12**, chrysenes; **13**, benzopyrenes and their hydrogenated compounds; and **14**, coke. Some representative constituents are shown in Table 4.

Table 4. Representative products identified by means of GC-MS

	Representative product
1	CH_4 C_2H_6 C_3H_8 n-and i-C_4H_{10} C_4H_8 C_3H_6
2	n-and i-C_5H_{12} 2,3-dimethylbutane 3-methylpentane
3	
4	
5	
6	
7[a]	
8[a]	
9	
10	
11	
12	

a) Phenanthrene-type compounds were not listed in this table.

Results and Discussion

Fractions II—IV are especially supposed to be better model substances for the hydrocracking of coals. The results of hydrocracking are shown in Table 5, along with the reaction conditions used. Table 6 describes the composition of the gaseous products (**1**: C_1—C_4 gases).

In the hydrocracking of Fraction II (Runs 1 and 2), the difference in the catalytic activity between zinc chloride and the binary mixture of zinc chloride and copper(I) chloride was examined. The yield of benzene and its derivatives (**4**) in Run 1 (14.6%) is lower than that in Run 2 (23.3%), and the combined yield of higher aromatics (**7**—**11**) in Run 2 (8.8%) is lower than that in Run 1 (28.7%). This result suggests that the catalytic activity of $ZnCl_2$/CuCl molten salt is superior to that of $ZnCl_2$. Since aromatic-type bonds are not expected to be thermally cleaved at 400 °C, the single C–C bonds of hydroaromatics are considered to be ruptured in the course of this hydrocracking. Therefore, it is necessary that aromatic rings be hydrogenated before they receive catalytic cracking by acidic molten salts. From this standpoint, the capabilities of both hydrogenation and cracking are demanded for the hydrocracking catalyst. On the basis of the product distribution, it is possible to estimate which acts predominantly in this hydrocracking. For example, the ratio of **5**/**6** is supposed to be a measure of the hydrogenating activity of the catalyst. The higher ratio of **5**/**6** in Run 2 than in Run 1 would demonstrate the improvement of its hydrogenating activity upon the addition of copper(I) chloride to zinc chloride. On the other hand, the ratio of isobutane to butane in the gaseous products was found to be not so changed by the addition of copper(I) chloride to zinc chloride. As the ratio of isobutane to butane is supposed to be a measure of the cracking activity of acidic molten salts, this finding shows that the intrinsic cracking activity of zinc chloride according to its Lewis acidity is not so much changed by this addition of copper(I) chloride. Kenney *et al.*[15] demonstrated that the catalytic activity of zinc chloride was lowered by

Table 5. Reaction conditions and results

Run No.		1	2	3	4	5	6	7	8
Feed (Fraction No.)		II	II	III	III	III	III	IV	IV
Catalyst		$ZnCl_2$	$ZnCl_2$/CuCl[a]	—	$ZnCl_2$	$ZnCl_2$	$ZnCl_2$/KCl[b]	$ZnCl_2$	$ZnCl_2$
Cat. ratio[c]		1.0	1.0	—	1.0	1.0	1.0	1.8	0.7
Initial hydrogen pressure (kg/cm²)		100	100	100	60	100	100	100	100
Products (wt%)	**1**	16.4	21.9	5.9	23.7	17.4	9.7	49.4	22.9
	2	3.6	5.6	tr	1.0	1.2	0.5	0.9	0.9
	3	14.6	16.8	0.1	4.8	7.0	2.7	5.4	5.3
	4	14.6	23.3	0.3	10.3	6.6	3.2	10.9	5.5
	5	13.3	14.5	0.6	5.6	6.6	4.2	6.5	7.9
	6	8.6	4.4	1.1	5.0	3.6	4.1	6.0	5.3
	7	12.9	4.1	7.1	5.6	8.1	11.5	3.9	5.3
	8	10.7	1.7	8.7	5.5	9.5	11.4	5.0	4.8
	9	1.6	0.6	21.9	1.9	6.1	7.6	0.7	2.9
	10	3.1	2.2	38.0	18.7	25.6	34.4	8.1	13.8
	11	0.4	0.2	9.5	2.3	4.9	7.3	0.4	4.8
	12	—	—	6.8	3.0	2.1	3.1	0.8	8.3
	13	—	—	—	—	—	—	1.7	11.4
	14	0.2	4.7	tr	12.6	1.3	0.3	0.3	0.9

a) $ZnCl_2$: CuCl=60: 40 (mol%); $ZnCl_2$+CuCl/Feed=1.0. b) $ZnCl_2$: KCl=60: 40 (mol%); $ZnCl_2$/Feed=1.0. c) Catalyst/Feed (mol/mol) average molecular weights were used.

Table 6. Composition of gases in **1** (wt%)

	Run No.							
	1	2	3	4	5	6	7	8
CH_4	8.5	9.7	25.7	15.2	8.4	20.0	20.0	15.7
C_2H_6	18.6	14.1	68.4	18.9	31.1	48.1	30.7	31.4
C_2H_4	—	—	—	2.0	—	—	—	—
C_3H_8	23.1	23.2	5.9	24.8	26.6	16.4	22.5	22.9
C_3H_6	—	—	—	2.9	—	—	—	—
i-C_4H_{10}	37.1	39.3	tr	22.4	21.9	2.9	12.5	8.2
n-C_4H_{10}	7.8	9.3	tr	7.3	4.1	12.6	9.2	16.1
C_4H_8	4.9	4.4	—	6.5	7.9	tr	5.1	5.7

the addition of metal chlorides, such as KCl, NaCl, and AgCl, in the hydrogen chloride elimination of isopropyl chloride; the principal exception was copper(I) chloride. In addition to the results similar to their findings, an improvement in the hydrogenating activity was found in this investigation. This synergenic effect of the addition of copper(I) chloride to zinc chloride was also found in the hydrocracking of anthracene,[16] phenanthrene, pyrene, fluoranthene, and chrysene.[17]

In the hydrocracking of Fraction III (Runs 3—6), the change in the cracking activity of zinc chloride caused by the addition of potassium chloride and the effect of the initial hydrogen pressure on the hydrocracking were examined. By comparing the result of Run 5 with that of Run 6, the binary mixture of $ZnCl_2$ and KCl was found not to display any appreciable catalytic activity. In the hydrocracking of hydroaromatics in this temperature range, two different reactions can occur.[6] The first of them is thermal cracking under a hydrogen atmosphere, which proceeds by means of a free radical mechanism; the other is catalytic cracking, which proceeds by means of a carbonium ion mechanism. When the hydrocracking proceeds by means of the latter mechanism, the ratio of iso to normal isomers is higher than that in a thermodynamic equilibrium. From this standpoint, the low yield of branched alkanes found in the case of Run 6 describes the lowering of the cracking activity of zinc chloride by the addition of potassium chloride. As the catalytic action of $ZnCl_2$ is attributed to its own molecular character, the formation of ionic complexes (such as K_2ZnCl_4) lowers the intrinsic cracking activity of molten zinc chloride. This is consistent with the result of Kenney *et al.*[15] In the absence of an acidic metal chloride (Run 3), small amounts of gases (most of them are methane and ethane) are obtained, and so the hydrogenation of aromatics is considered to govern this reaction. The effect of the hydrogen pressure is also shown in Runs 4 and 5. At higher hydrogen pressures, the formation of coke is found to be suppressed to a significant extent. This result indicates that the formation of coke may proceed *via* intermolecular dehydrogenation, and that hydrogen may act to capture active intermediates, such as species leading to coke with lesser amounts of hydrogen. The reason for the lowering of cracked products at higher hydrogen pressures may also be attributed to this stabilization.

The quantity of the catalyst is one of the most important factors dominating this hydrocracking (Runs 7 and 8). For example, the change in the conversion according to the quantity of the catalyst is remarkable in the yields of gaseous products. From this finding, the lowering in the cracking activity upon the addition of potassium chloride to zinc chloride mentioned above is attributable to the decrease in the amounts of effective parts of the catalyst.

In all the runs, *cata*-condensed polycyclic aromatics (anthracenes, phenanthrenes and chrysenes) were hydrocracked more efficiently than *peri*-condensed polycyclic aromatics (pyrenes). Therefore, benzopyrenes were hydrocracked to pyrenes, which were relatively resistant to the hydrocracking in the molten salt catalyst. Also, the reactivity of fluoranthenes was found to be fairly high.

In the hydrocracking of Fraction IV with a higher S content, the behavior of S was examined. Most of the S was found in the form of zinc sulfide. Attention was not given to the behavior of N and O, but the contents of hetero atoms in the products were found to be lower than in the feed.

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