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STUDIES ON HYDROCRACKING OF COAL RELATED SUBSTANCES OVER MOLTEN SALT CATALYSTS

(溶融塩触媒を用いた石炭関連物質の
水素化分解に関する研究)

1979

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PREFACE

This thesis was performed under the guidance by Professor Shōichi Kikkawa at the Department of Applied Chemistry, Faculty of Engineering, Osaka University.

This thesis describes the hydrocracking of a series of coal related substances over molten salt catalysts mainly consisting of zinc chloride. The honor would be entirely mine, if the findings presented in this work would make an ounce of contribution to the fundamental study of coal.

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January, 1979

CONTENTS

CHAPTER 1

General Introduction

Since the so-called oil shock in 1973, coal has been reassessed as an important source of energy or hydrocarbons which will replace petroleum. As coal-producing districts are impartial and coal deposits are greatly larger than oil deposits, the development of the effective utilization methods of coal is a very important problem, above all, hydrocracking has been watched as one of the most practical methods all over the world (especially in U.S.A.).

Although the detailed structure of coal has never been clarified, some structural analyses suggest that coal is the natural polymer possessing several structural units consisted of mainly condensed rings. Consequently, in order to obtain liquid fuels from coal, it is desirable to use the catalyst which accelerate the decomposition of the condensed rings in addition to the scission of the bonds between the structural units.

In view of this background and standpoint, this work was carried out for the purpose of developing a new catalyst system of coal liquefaction and obtaining the fundamental findings of coal research.

The new catalyst system was prepared by the addition of metal chloride to zinc chloride which has been expected as a promising catalyst for coal. In order to obtain the fundamental data with regard to the catalytic action of molten salts for coal, it is convenience to use model substances. The chracteristics of the model substances used in this study were as follows: 1) A heavy anthracene oil (Chapter 2): This is considered to be a mixture of many polynuclear aromatic hydrocarbons. The general catalytic activity of molten salts will be deduced on the product distribution. 2) A pure substance (Chapters 3 and 4): The properties of the starting material are known and the reaction process will be easily deduced. 3) Solvent refined coal (Chapter 5):

This is considered to be representative of structure of coal.

This thesis will describe the results obtained from the hydrocracking of coal related substances mentioned above and Yūbari coal (Chapter 6) in the presence of the molten salt catalysts.

The contents of this thesis are composed of the following papers.

1) Active molten salts catalyst for hydrocracking of anthracene
S.Kikkawa, M.Nomura, T.Kubo, and Y.Nakatsuji, Chem.Lett., 1976, 1383.
2) The hydrocracking of a heavy anthracene oil over molten salt catalysts
Y.Nakatsuji, S.Fujioka, M.Nomura, and S.Kikkawa,
Bull.Chem.Soc.Jpn., 50, 3406 (1977).
3) The hydrocracking of polynuclear aromatic hydrocarbons over molten salt catalysts
Y.Nakatsuji, T.Kubo, M.Nomura, and S.Kikkawa,
Bull.Chem.Soc.Jpn., 51, 618 (1978).
4) The hydrocracking of alkyl-substituted polynuclear aromatic hydrocarbons over $ZnCl_2$/CuCl molten salt catalyst
Y.Nakatsuji, Y.Ikkaku, M.Nomura, and S.Kikkawa,
Bull.Chem.Soc.Jpn., 51, 3631 (1978).
5) Hydrogenation of Japanese coals supported with metal halides
T.Ida, M.Nomura, Y.Nakatsuji, and S.Kikkawa, Fuel, in contribution.
6) The hydrocracking of solvent refined coals over molten salt catalysts
Y.Nakatsuji, Y.Ikkaku, M.Nomura, and S.Kikkawa,
Bull.Chem.Soc.Jpn., in contribution.

CHAPTER 2

The Hydrocracking of a Heavy Anthracene Oil over Molten Salt Catalysts

2-1 INTRODUCTION

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.(1,2) 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 standpoint of view, the hydrocracking of model compounds, which are supposed to be constituent units of coal, has been investigated.(2-11) Zielke et al.(4) 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.(12) As a part of this study, the hydrocracking of a heavy anthracene oil, which thus seems to be a kind of model substance, will be described in this chapter. In addition, the change in the hydrocracking activity of zinc chloride by the addition of another metal chloride will be shown.

2-2 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 20eV connected with a Hitachi M 5201 apparatus using a 3m x 3mm 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.

(1) Characterization of Feed.

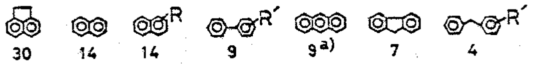
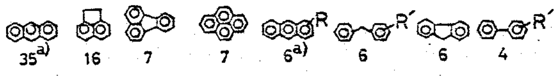
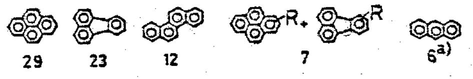
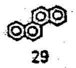
A heavy anthracene oil (obtained from Osaka Gas Co.,Ltd.; Specific gravity (50/4°C) 1.142; moisture 0.5%; distillation test (dehydrated sample) 0-360°C: 28.0%) was separated into three fractions and a residue by means of vacuum distillation. The characterization of these fractions is shown in Tables 2-1 and 2-2.

Table 2-1. 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

Table 2-2. 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.

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[13)] (Table 2-3) gave results in good agreement with the results based on the information obtained from GC-MS.

Table 2-3. Type Analyses 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

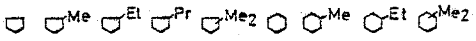
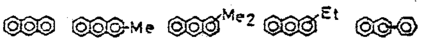
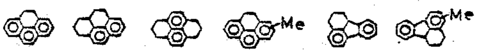
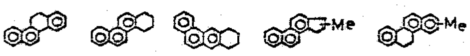
(2) Genaral Procedure.

All the experiments were carried out in a stainless steel (SUS 32) autoclave with a capacity of 500ml, shaken in a horizontal direction (70 strokes/min). A stainless steel vessel containing feed (about 20g) 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 3h. After the system had been cooled to room temperature, gases were admitted into a gas holder and analyzed by GLC (60-80mesh Silica gel column 3m x 3mm). Solid samples from the reaction products were dissolved in a proper solvent and analyzed by GLC (4.5m x 3mm column packed with 20% SE-30 on Uniport B 60-80mesh). 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 thiosulfate solution.

(3) Analysis of Products.

The prodcuts were mainly identified 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 2-4.

Table 2-4. 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.

2-3 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 2-5, along with the reaction conditions used. Table 2-6 describes the composition of the gaseous products (1: C_1-C_4 gases).

Table 2-5. 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/cm^2)		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 2-6. 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

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 are 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.[14)] demonstrated that the catalytic activity of zinc chloride was lowered by 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, as an improvement in the hydrogenating activity was found in this investigation.

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.5) 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.14) 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 pressure, 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 pressure 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 effectively 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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CHAPTER 3

The Hydrocracking of Polynuclear Aromatic Hydrocarbons over Molten Salt Catalysts

3-1 INTRODUCTION

The hydrocracking of the model compounds, which are supposed to be structural units of coal, has frequently been carried out in order to examine the function of catalysts and the reaction process. In the investigation reported by Qader,1) the hydrocracking of naphthalene, anthracene, and pyrene was found to proceed through a sequential occurence of hydrogenation, isomerization, and cracking reactions over silica-alumina-based dual-functional catalysts, which are extensively used in the industrial processing of petroleum feedstocks. Zielke et al.2) had shown molten zinc chloride to be a superior acidic catalyst for the hydrocracking of pyrene and coal extracts when used in high concentrations.

As a part of a study of organic reactions in molten salts,3) the catalytic activity of molten salts was examined in the hydrocracking of a heavy anthracene oil. In the experiment, a binary mixture of $ZnCl_2$ and CuCl was found to be more effective than $ZnCl_2$ alone in obtaining many lower-boiling fractions; both the analysis of the starting oil and the confirmation of the products were also carried out extensively. However, in the hydrocracking of the heavy anthracene oil, the behavior of the representative constituents of the starting oil, that is, anthracene, phenanthrene, chrysene, pyrene, and fluoranthene, could not clarified in detail. Concerning the hydrocracking of anthracene, the efficient catalytic activity of the binary mixture of $ZnCl_2$ and CuCl was reported in a preliminary paper.4) In addition to the above results, this chapter will describe the application of this catalyst to the hydrocracking of phenanthrene, chrysene, pyrene, and fluoranthene and their characteristic properties. The effects of two different-batch autoclave systems on their product distributions are also investigated. Moreover, the probable reaction routes for the respective reactions of phenanthrene, chrysene, and fluoranthene will be offered and discussed.

3-2 EXPERIMENTAL

(1) Product Analysis.

The GLC analyses were performed on a Shimadzu GC-3AH for the gaseous products and on a Shimadzu GC-4BPTF for the liquid and solid products. The GC-MS spectra were taken at 20eV with a Hitachi RMU-6MG spectrometer connected with a Hitachi M 5201 gas chromatograph by using a 3m x 3mm column of 5% Silicone OV-1 on Uniport KS. The main products were isolated on a Shimadzu GC-3BT using a 3m x 3mm column of 10% Pluronic L 84 on Neopack IA (for products from phenanthrene) or a 3m x 3mm column of 20% Silicone DC 550 on Celite 545 (for products from pyrene, chrysene, and fluoranthene). The NMR spectra were recorded on a Jeol JNM-PS-100 spectrometer, using tetramethylsilane as the internal standard. CCl_4 was used as the solvent for all the compounds. The UV spectra and the IR spectra were taken with a Hitachi 124 spectrometer and a Jasco IR-E spectrometer respectively.

(2) Materials.

The chrysene (G.R.), fluoranthene (E.P.), and phenanthrene (E.P.) were obtained from the Tokyo Kasei Kogyo Co.,Ltd. The pyrene (G.R.) and anthracene (E.P.) were obtained from Nakarai Chemicals,Ltd., and Wako Pure Chemical Industries,Ltd., respectively. The anthracene and phenanthrene were recrystallized from ethanol. The fluoranthene (98% purity by GLC) contained a small amount of cyclopenta[j,k]phenanthrene. This impurity was not removed before use. The zinc iodide and copper(I) bromide were obtained from the

Mitsuwa Chemicals Co.,Ltd., while the other metal halides used in this investigation were obtained from Nakarai Chemicals,Ltd. These salts were dried before use at 400°C for 1h in nitrogen.

(3) Genaral Procedure.

All the experiments were carried out in the two different systems (A and B) as follows:

A) A stainless steel vessel containing 8g of feed and an equimolar amount of the catalyst was placed in a stainless steel (SUS 32) autoclave with a capacity of 200ml. The system was flushed and filled with hydrogen to 100 kg/cm^2; then the autoclave was heated up to the desired temperature. The time taken to reach the stage was from 60 to 70min. The reaction system shaken in a horizontal direction (68strokes/min) was maintained at 400°C for the desired reaction period. No attempts were made to maintain the hydrogen pressure at a constant level during the reaction.

B) A stainless steel vessel containing 10g of feed and an equimolar amount of the catalyst was placed in a stainless steel (SUS 32) autoclave with a capacity of 500ml. Hydrogen was introduced into the autoclave to 100kg/cm^2. The rate of the temperature rise was controlled to about 3°C/min up to 400°C, after which the temperature was held for the desired reaction period. The autoclave was shaken in a horizontal direction (70strokes/min). No attempts were made to maintain the hydrogen pressure at a constant level during the reaction.

After the system (A or B) had been cooled to room temperature, gases were collected in a gas holder and analyzed by GLC (60-80mesh Silica gel column). When the products were obtained in a solid state, they were dissolved in a proper solvent and analyzed by GLC (4.5m x 3mm packed with 20% SE-30 on Uniport B 60-80mesh, programmed from 30-270°C, 5°C/min, TCD, H_2 Carrier).

The products obtained in a liquid state were also analyzed by GLC in neat. The actual quantitative interpretation of a chromatogram is based on the peak area. The weight correction factors were determined by the measurement of the relative areas of authentic compounds. The values conveniently used in this study were as follows: retention time, 0-11 min, 0.9; 11-32min, 1.0; 32-37min, 1.1; 37-42min, 1.2; 42-50min, 1.3; 50min- , 1.4 (Figs.3-1 ÷ 3-5). The mixture of coke and catalyst obtained after the extraction of the products was washed with hydrochloric acid in order to remove the catalyst. The coke obtained in this manner was dried and weighed.

(4) Classification of Products.

In order to characterize the activity of molten salt catalysts, the products were conveniently classified into 27 groups as follows: I, C_1-C_4 gases; II, C_5-C_7 alkanes; III, cycloalkanes; IV, monocyclic aromatics; V, indans and tetralins; VI, bicyclic aromatics; VII, dihydrophenanthrene; VIII, tetrahydrophenanthrene and its isomers; IX, octahydrophenanthrene and its isomers; X, phenanthrene; XI, higher-boiling compounds; XII, coke; XIII, benzindans, tricyclic aromatics, and their hydrogenated compounds; XIV, perhydropyrenes; XV, decahydropyrenes; XVI, tetrahydropyrene; XVII, hexahydropyrenes; XVIII, dihydropyrene; XIX, pyrene; XX, dodecahydrochrysene and its isomers; XXI, octahydrochrysene and its isomers; XXII, dihydrochrysene; XXIII, hexahydrochrysene and its isomers; XXIV, tetrahydrochrysene and its isomers; XXV, chrysene; XXVI, tetrahydrofluoranthene; XXVII, fluoranthene.

3-3 RESULTS AND DISCUSSION

(1) Identification of Products.

The mass spectra of all the products in this study were obtained by means of GC-MS. The molecular weights of the products are given, and the chemical structures can be fairly deduced when specific cleavage patterns are found in the mass spectra. The results of the identification of the hydrocracked products of anthracene by considering their mass spectra in combination with the eluted order on the gas chromatogram estimated from their boiling products were previously published.5) In that case, the isomerization of the skeleton of anthracene seemed not to occur. However, the isomerization between sym-octahydroanthracene and sym-octahydrophenanthrene was clearly found in this hydrocracking of anthracene over acidic molten salts,4,6) so additional analytical methods were considered necessary for more detailed analyses. The main products were isolated by preparative GLC and analyzed by using NMR spectrometry. The NMR spectral data obtained for the isolated products were as follows: 6-butyltetralin, δ=0.92(3H,t), 1.08-1.68(4H,m), 1.78(4H,m), 2.46 (2H,t), 2.66(4H,m), and 6.6-7.0(3H,m); 1,2,3,4,4a,9,10,10a-octahydrophenanthrene, 6.90(4H,s); 1,2,3,4,5,6,7,8-octahydrophenanthrene, 1.75(8H,m), 2.48(4H,m), 2.65(4H,m), and 6.60(2H,s); 9,10-dihydrophenanthrene, 2.81(4H,s), 7.02-7.33 (6H,m), and 7.48-7.72(2H,m); 1,2,3,4-tetrahydrophenanthrene, 1.82(4H,m), 2.88 (2H,m), 3.07(2H,m), and 6.96-7.96(6H,m); 1,2,3,3a,4,5,9,10,10a,10b-decahydropyrene, 6.5-7.0(3H,m); 1,2,3,3a,4,5,5a,6,7,8-decahydropyrene, 6.64(2H,s); 4,5,9,10-tetrahydropyrene, 2.84(8H,s) and 6.92(6H,s); 1,2,3,3a,4,5-hexahydropyrene, 1.2-2.4(6H,m), 2.6-3.4(5H,m), and 6.8-7.7(5H,m); 1,2,3,6,7,8-hexahydropyrene, 2.01(4H,m), 3.0(8H,t), and 6.92(4H,s); 4,5-dihydropyrene, 3.24 (4H,s) and 7.16-7.68(8H,m); 5,6,8,9,10,11-hexahydrobenz[a]anthracene, 1.80 (4H,m), 2.72(8H,m), and 6.76-7.80(6H,m); 1,2,3,4,5,6-hexahydrochrysene, 1.84 (4H,m), 2.73(8H,m), and 6.8-7.7(6H,m); 8,9,10,11-tetrahydrobenz[a]anthracene, 1.80(4H,m), 2.92(4H,m), and 7.3-8.6(8H,m); 1,2,3,4-tetrahydrochrysene, 1.96 (4H,m), 2.94(2H,m), 3.16(2H,m), and 7.2-8.8(8H,m); 5,6-dihydrochrysene, 2.86 (2H,m), 3.20(2H,m), and 6.8-8.1(10H,m); 6-phenyltetralin, 1.82(4H,m), 2.77 (4H,m), and 6.9-7.6(8H,m); 5-phenyltetralin, 1.76(4H,m), 2.56(2H,m), 2.80

(2H,m), and 6.8-7.5(8H,m). When the NMR spectrum of an isolated compound is complicated, the information about the molecular weight obtained from the mass-spectral measurements and the ratio of aromatic hydrogen to non-aromatic hydrogen from the NMR method often gave the correct structure (e.g., the distinction between 1,2,3,3a,4,5,9,10,10a,10b-decahydropyrene and 1,2,3,3a,4,5,5a,6,7,8-decahydropyrene). When the amount of a compound isolated was small, UV spectrometry was conventionally used for the structural confirmation. The type of aromatic hydrocarbon (that is, benzene, naphthalene, biphenyl, anthracene, phenanthrene, pyrene, fluoranthene, chrysene, and so on) is clarified based on the characteristic absorption bands. For example, the absorption wave numbers of phenanthrene, 4,5-dihydropyrene, 1,2,3,4-tetrahydrochrysene, and 8,9,10,11-tetrahydrobenz[a]anthracene differed to some degree, but their characteristic absorption bands were similar. This indicates that these compounds all have a phenanthrene skeleton. Of course, IR spectrometer played an important role in the analysis. The cleavage patterns of the mass spectra of the compounds identified by using these analytical methods could then be applied to other compounds. The GC charts of the hydrocracked products are shown in Figs. 3-1 - 3-5, where the structures chracterized or assumed are listed. The structures of benzindan derivatives and their hydrogenated compounds are not certain because the distinction between 2,3-dihydro-1H-benz[e]indene and 2,3-dihydro-1H-benz[f]indene is not clear only by considering their mass spectra. Consequently, the structures for these compounds listed in these figures are chosen for convenience. By this exhaustive analysis, the probable reaction process can be estimated and the difference in catalytic activity among the molten salt catalysts can be clarified.

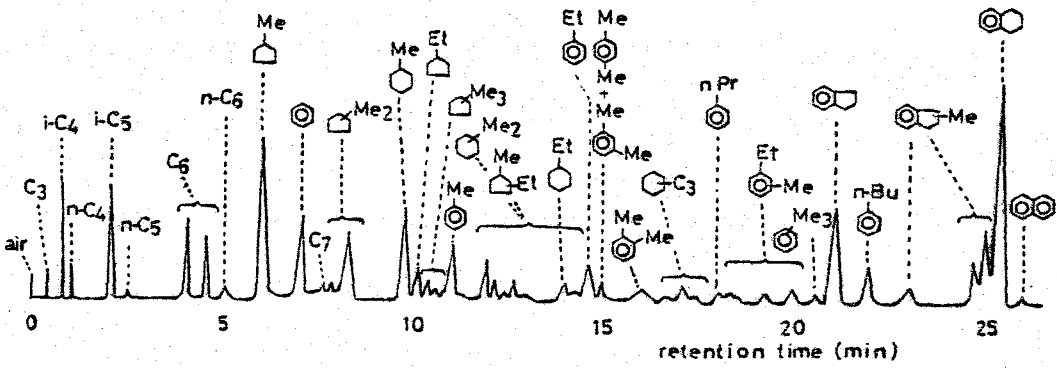

Fig. 3-1. Gas Chromatogram of Hydrocracked Products of Polynuclear Aromatic Hydrocarbons

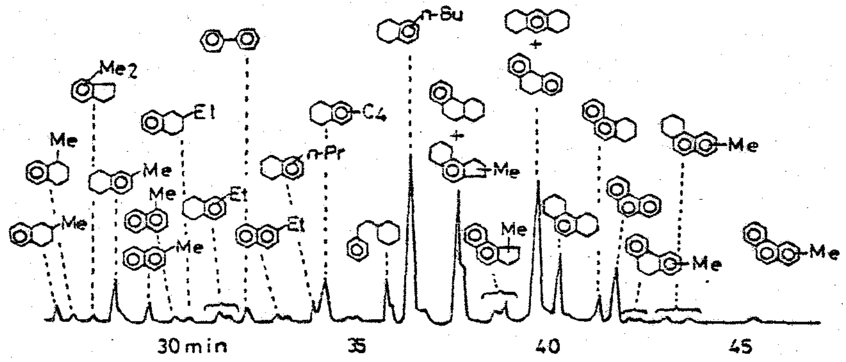

Fig. 3-2. Gas Chromatogram of Hydrocracked Products of Phenanthrene

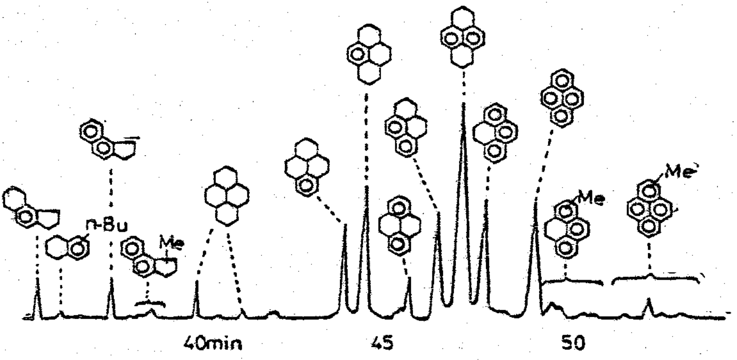

Fig. 3-3. Gas Chromatogram of Hydrocracked Products of Pyrene

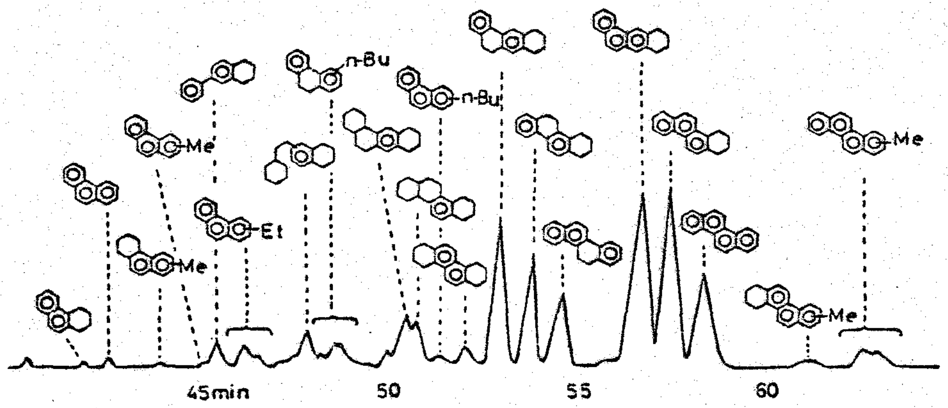

Fig. 3-4. Gas Chromatogram of Hydrocracked Products of Chrysene

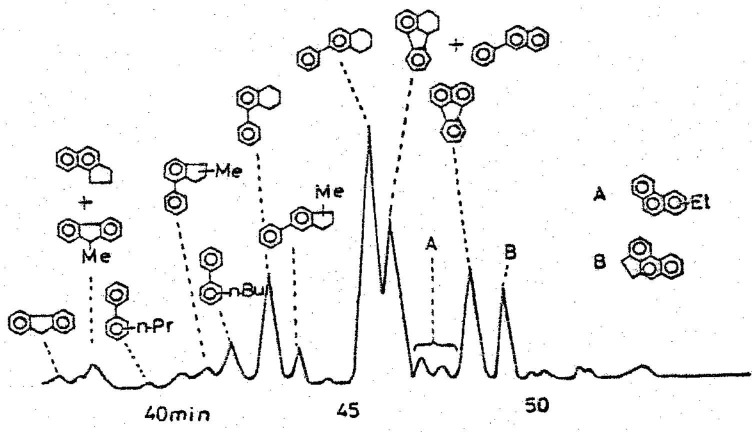

Fig. 3-5. Gas Chromatogram of Hydrocracked Products of Fluoranthene

(2) Hydrocracking of Phenanthrene.

The most probable reaction process is shown in Fig.3-6. The most important characteristic of the hydrocracking of phenanthrene is the isomerization between sym-octahydrophenanthrene and sym-octahydroanthracene. The isomerization was also found in the hydrocracking of anthracene in the presence of a Lewis acid.4,6) A constant ratio of them in equilibrium was observed, so this isomerization is considered to be reversible. This finding is consistent with that observed over aluminum chloride by Schroeter.7) On the other hand, this isomerization was not observed in their hydrogenation in the presence of alkali metals.8) These findings suggest that the decomposition

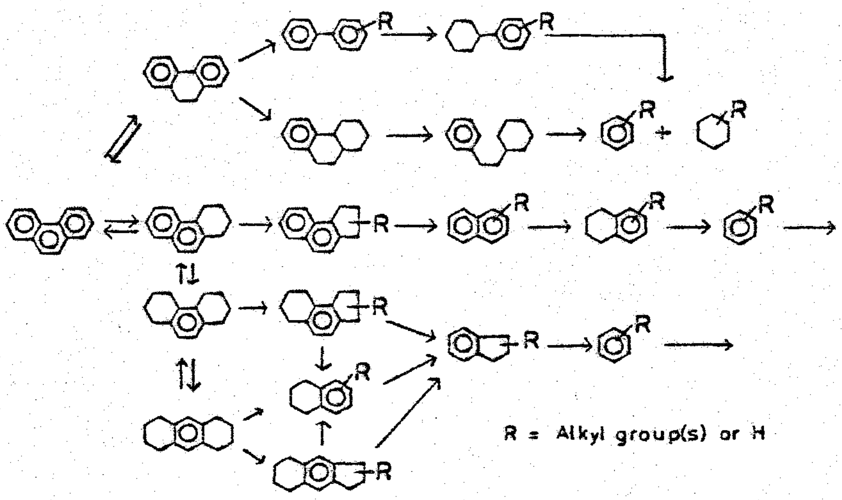

Fig. 3-6. Probable Reaction Process of Phenanthrene

process of sym-octahydroanthracene must also be considered in the hydrocracking of phenanthrene over acidic catalysts.

The formation of 1-cyclohexyl-2-phenylethane was found in the products [δ=2.56(2H,t,J=8Hz)]. unsym-Octahydrophenanthrene is considered to be cleaved and hydrogenated to that compound, judging from the similarity of the structures of these two compounds. In the presence of aluminum chloride, secondary alkylbenzene was dealkylated in preference to primary alkylbenzene.9) If this finding is extended to the case of unsym-octahydrophenanthrene, the preferable scission of its C_{4a}-C_{4b} bond to produce 1-cyclohexyl-2-phenylethane may be reasonable. Although the above decomposition process has never been indicated in this connection, it is one of the most important decomposition routes in the hydrocracking of phenanthrene.

The product distributions are shown in Table 3-1. From the standpoint of the distribution of gaseous products, especially the ratio of iso to normal isomers, the catalytic action of molten salts was discussed in chapter 2. The constituents of the gaseous products in Run 2 were as follows: methane, 8.0wt%; ethane, 7.5%; propane, 33.6%; isobutane, 38.0%; butane, 9.3%; butenes, 3.6%.

Table 3-1. Hydrocracking of Phenanthrene

Reaction conditions: initial hydrogen pressure, 100 kg/cm^2; reaction temperature, 400 °C; reaction system A: Catalyst/Feed = 1.0 (mol/mol), Hydrogen/Feed = 18.8 (mol/mol); B: Catalyst/Feed = 1.0, Hydrogen/Feed = 26.7.

		Run No.						
		1	2	3	4	5	6	7
Catalyst (mol : mol)		$ZnCl_2$	$ZnCl_2/CuCl$ (60:40)	ZnI_2/KI (80:20)	$ZnCl_2/NiCl_2$ (90:10)	—	$ZnCl_2$	$ZnCl_2/CuCl$ (60:40)
Reaction system		A	A	A	A	B	B	B
Reaction time (h)		3	3	3	3	1	1	1
Product (wt %)	I	0.4	27.7	0.2	11.2	2.0	1.6	3.2
	II	—	7.2	—	1.4	—	—	0.3
	III	—	7.0	0.1	7.5	—	—	2.2
	IV	0.1	33.2	—	10.5	—	0.3	3.3
	V	0.1	12.4	2.2	11.5	0.1	0.9	10.9
	VI	0.4	2.2	0.1	1.0	0.6	0.4	0.6
	VII	8.0	0.5	14.2	9.8	13.6	21.2	14.8
	VIII	3.5	1.4	13.7	6.9	5.7	9.5	7.5
	IX	—	1.1	5.2	4.8	3.5	7.0	22.6
	X	87.5	1.4	63.4	33.4	74.5	55.5	24.9
	XI	—	1.3	0.9	2.0	—	3.2	5.0
	XII	—	4.6	—	—	—	0.4	4.7

Since the ratio of isobutane to butane is higher than that in the thermodynamic equilibrium, this hydrocracking is considered to proceed by means of a carbonium-ion mechanism.10)

The catalytic activity of the binary mixture of zinc iodide and potassium iodide is superior to that of zinc chloride in the hydrogenation of phenanthrene (Runs 1 and 2). In this case, attention must be paid to the fact that the intrinsic cracking activity is lowered by the addition of potassium iodide because of the formation of the complex ions.11) The conversion in the presence of the zinc chloride containing 10mol% nickel(II) chloride is lower than that in the presence of zinc chloride containing 40mol% copper(I) chloride, but the product distributions obtained over these two catalysts are similar (Runs 2 and 4). Therefore, the decomposition process of phenanthrene over $ZnCl_2/NiCl_2$ is considered to be intermediate between that over $ZnCl_2$ and that over $ZnCl_2/CuCl$. This finding suggests that zinc chloride has a good intrinsic cracking activity under these reaction conditions, but its hydrogenating activity is not so high. The addition of a good hydrogenating catalyst to zinc chloride will produce an excellent catalyst for the hydrocracking of polynuclear aromatic hydrocarbons. Consequently, these molten salt catalysts act as dual-functional catalysts, and appropriate molten mixtures of metal salts with the hydrogenating activity may be able to become effective catalysts.

A remarkable catalytic action of $ZnCl_2/CuCl$ was observed in this investigation (Runs 1 and 2). The hydrogenating activity of zinc chloride is very low in this temperature range (Run 1). The intrinsic cracking activity of zinc chloride may not be able to operate because phenanthrene is little hydrogenated. The addition of copper(I) chloride to zinc chloride must contribute to the improvement of the hydrogenating activity of the catalyst. The difference in the yield of octahydrophenanthrene and its isomers (IX) between Run 6 and Run 7 indicates this improvement in the hydrogenating activity.

By comparing the results of Run 1 and Run 6, phenanthrene was found to be more hydrogenated in Run 6 than in Run 1. From this fact, it can be seen that the ratio of hydrogen to the feed must affect the product distributions. In addition, the material, the capacity, the stirring pattern, and the memory effect of the autoclave are also important factors in dominating these reactions. Therefore, even if the pressure, the temperature, and the ratio of hydrogen to the feed should be maintained at constant levels in the different systems, similar results may not be obtained.

(3) Hydrocracking of Pyrene.

Pyrene is liable to accept the hydrogenation (Runs 1 and 9), but is fairly stable to the catalytic cracking (Runs 2 and 10), compared with phenanthrene. If the decomposition of dihydropyrene to phenanthrene takes place, the hydrocracking may occur easily. In practice, however, dihydropyrene was converted further to highly hydrogenated pyrenes, and so the probable

Table 3-2. Hydrocracking of Pyrene

Reaction conditions: initial hydrogen pressure, 100 kg/cm^2; reaction temperature, 400 °C; reaction system A: Catalyst/Feed=1.0 (mol/mol), Hydrogen/Feed=21.3; reaction system B: Catalyst/Feed=1.0, Hydrogen/Feed=30.5.

		Run No.						
		8	9	10	11	12	13	14
Catalyst (mol: mol)		—	$ZnCl_2$	$ZnCl_2/CuCl$ (60:40)	ZnI_2/KI (80:20)	$ZnBr_2/CuBr$ (60:40)	$ZnCl_2$	$ZnCl_2/CuCl$ (60:40)
Reaction system		A	A	A	A	A	B	B
Reaction time (h)		3	3	3	3	3	3	3
Product (wt %)	I	—	0.7	13.7	—	22.8	6.4	11.3
	II	—	—	1.1	—	4.4	0.3	2.5
	III	—	—	1.9	—	9.7	2.9	6.3
	IV	—	—	3.0	—	5.1	2.0	3.8
	V	—	—	3.2	—	4.3	2.1	5.7
	VI	—	—	tr	—	tr	0.2	0.1
	XIII	0.5	0.4	3.6	1.6	5.6	2.1	3.2
	XIV	—	—	1.2	3.5	2.3	4.3	4.8
	XV	—	1.5	7.5	16.7	4.5	20.4	14.4
	XVI	1.0	3.0	2.6	3.5	1.5	4.3	3.5
	XVII	3.6	8.5	21.3	40.4	7.7	31.1	20.9
	XVIII	16.7	23.7	13.5	15.8	4.3	9.6	7.8
	XIX	78.2	62.2	19.7	18.5	4.6	8.5	6.0
	XI	—	—	3.9	—	2.2	4.8	8.2
	XII	—	—	3.8	—	21.0	1.0	1.5

decomposition routes of pyrene could not be clarified in detail in this investigation. In the hydrocracking of pyrene, a binary mixture of zinc bromide and copper(I) bromide was used for the purpose of examining the effect of the difference of halide (Run 12). A high catalytic activity was found, but a fairly large amount of coke was also formed. This is probably the reason why the reaction conditions are not adequate for this catalyst. There is still much room for an examination of the reaction conditions. No remarkable difference in the product distributions of Runs 13 and 14 was observed because the large amount of hydrogen and the other factors mentioned above might serve to make uniform the characteristics of these two catalysts. This may be considered to be indirect evidence for the improvement of the hydrogenating activity by the addition of copper(I) chloride. The binary mixture of zinc iodide and potassium iodide displayed an excellent hydrogenating activity and a lack of the cracking activity (Run 11).

(4) Hydrocracking of Chrysene.

Table 3-3. Hydrocracking of Chrysene

Reaction conditions: initial hydrogen pressure, 100 kg/cm^2; reaction temperature, 400 °C; reaction system A: Catalyst/Feed=1.0, Hydrogen/Feed=24.1; reaction system B: Catalyst/Feed=1.0, Hydrogen/Feed=34.4.

		Run No.			
		15	16	17	18
Catalyst		ZnCl$_2$	ZnCl$_2$/CuCl	ZnCl$_2$	ZnCl$_2$/CuCl
(mol: mol)			(60:40)		(60:40)
Reaction system		A	A	B	B
Reaction time (h)		3	3	3	3
Product (wt %)	I	2.3	28.2	6.7	7.0
	II	—	10.7	—	3.7
	III	—	17.6	1.3	19.5
	IV	—	25.2	0.6	8.3
	V	0.4	10.1	4.5	24.1
	VI	—	1.0	0.6	2.2
	XIII	3.6	3.4	12.0	24.3
	XX	—	—	5.1	4.0
	XXI	2.3	0.3	2.9	0.5
	XXII	8.6	—	7.5	0.2
	XXIII	7.3	0.3	14.8	2.2
	XXIV	11.3	0.4	26.0	2.0
	XXV	64.2	0.1	9.2	—
	XI	—	—	7.7	—
	XII	—	2.7	1.1	2.0

The results of the hydrocracking of chrysene are shown in Table 3-3. Chrysene is hydrogenated to hydrochrysenes, which then isomerize to hydrobenz[a]anthracenes (Fig.3-7). For example, 1,2,3,4,5,6-hexahydrochrysene (containing a sym-octahydrophenanthrene skeleton) isomerizes to 5,6,8,9,10,11-hexahydrobenz[a]anthracene (containing sym-octahydroanthracene skeleton) in the presence of a Lewis acid. The formation of 8,9,10,11-tetrahydrobenz[a]anthracene is attributed to either the isomerization of 1,2,3,4-tetrahydrochrysene or the dehydrogenation of 5,6,8,9,10,11-hexahydrobenz[a]-

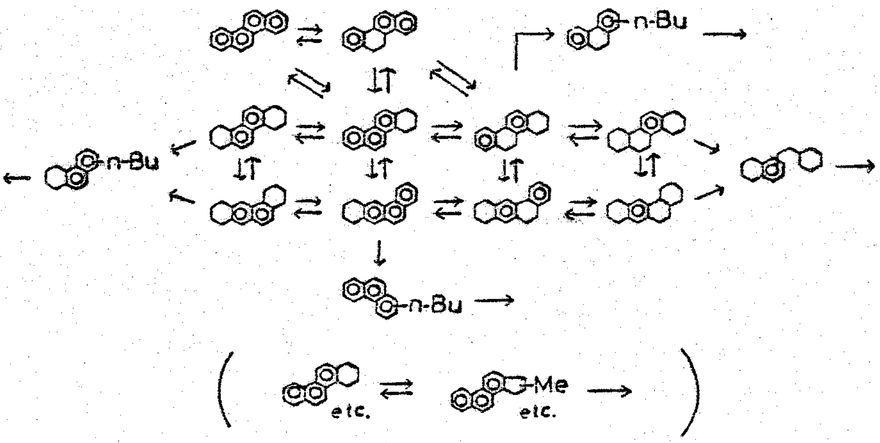

Fig. 3-7. Probable Reaction Process of Chrysene

anthracene; it is not certain which ocurred in practice. The main decomposition pathways of hydrochrysenes and their isomers are probably the formation of butylphenanthrene and the hydrogenated compounds. These phenanthrene-type compounds are hydrocracked in a manner similar to that described in the hydrocracking of phenanthrene. The decomposition route from dodecahydrochrysene and benz[a]anthracene to 5- and 6-(2-cyclohexylethyl)tetralin respectively becomes fairly important in the B system (Run 18), because the extent of the hydrogenation is relatively high. Of course, the saturated six-member rings of tetra-, octa-, dodecahydrochrysenes, and hydrobenz[a]anthracenes isomerize to five-member rings. The probable reaction process of chrysene is shown in Fig.3-7. A high catalytic activity of $ZnCl_2/CuCl$ was also observed in the hydrocracking of chrysene. Chrysene accepts hydrogenation relatively easily in comparison with phenanthrene (Runs 1 and 15).

(5) Hydrocracking of Fluoranthene.

In order to examine the initial decomposition process of fluoranthene, 1h was used as the reaction time. The results are shown in Table 3-4. The tetrahydrofluoranthene formed by the hydrogenation of fluoranthene is ruptured to 5-phenyltetralin in the presence of hydrogen, followed by isomerization to 6-phenyltetralin. Consequently, the amounts of biphenyl derivatives were fairly large. The great formation of biphenyls in the hydrocracking of a heavy anthracene oil may be attributed to this decomposition pathway. The decomposition process of fluoranthene is shown in Fig.3-8.12)

Table 3-4. Hydrocracking of Fluoranthene

Reaction conditions: initial hydrogen pressure, 100 kg/cm²; reaction temperature, 400 °C; reaction system A: Catalyst/Feed=1.0, Hydrogen/Feed=21.3; reaction system B: Catalyst/Feed=1.0, Hydrogen/Feed=30.5.

	Run No.	
	19	20
Catalyst (mol: mol)	$ZnCl_2$	$ZnCl_2/CuCl$ (60:40)
Reaction system	A	A
Reaction time (h)	1	1
I	—	14.9
II	—	3.3
III	—	5.8
IV	—	10.4
V	—	7.9
VI	—	5.4
XIII	2.4	31.5
XXVI	15.6	4.2
XXVII	80.4	5.2
XI	1.6	6.1
XII	—	5.3

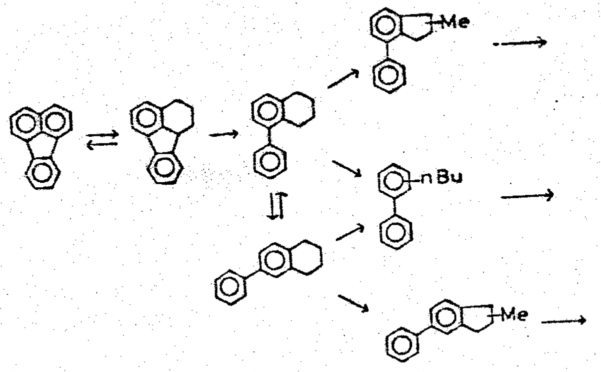

Fig. 3-8. Probable Reaction Process of Fluoranthene

(6) Hydrocracking of Anthracene.

The details of the hydrocracking of anthracene have been reported in a preliminary study.4) Anthracene is more easily hydrogenated than phenanthrene. The product distribution of anthracene is similar to that of phenanthrene when the hydrocracking proceeds to some degree. This phenomenon is attributable to the fact that the marginal hydrogenated ring is ruptured in preference to the central ring in a dihydro derivative, for the cleavage of a saturated single C-C bond of dihydroanthracene or phenanthrene should result in a different type of compound. In addition, it is necessary to take into account the fact that the isomerization between sym-octahydroanthracene and sym-octahydrophenanthrene does away with the difference in their product distributions.

3-4 CONCLUSION

Concerning the reaction routes over these molten salt catalysts, the findings in this investigation may be outlined as follows: 1) the isomerization between sym-octahydrophenanthrene and sym-octahydroanthracene in the hydrocracking of phenanthrene and anthracene, and a similar isomerization in the hydrocracking of chrysene; 2) the decomposition of unsym-octahydrophenanthrene to 1-cyclohexyl-2-phenylethane in the hydrocracking of phenanthrene and a similar cleavage in the hydrocracking of chrysene; 3) a decomposition pathway leading to biphenyls in the hydrocracking of fluoranthene. On the other hand, $ZnCl_2/CuCl$ molten salt, which is considered to act as a dual-functional catalyst, displayed a more efficient catalytic activity for cata-condensed aromatic hydrocarbons (phenanthrene, anthracene, and chrysene) than for peri-condensed aromatic hydrocarbons (pyrene). Moreover, these results (listed in Figs.3-1 - 3-5) were useful in the identification of the hydrocracked products of Yūbari coal.14)

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CHAPTER 4

The Hydrocracking of Alkyl-substituted Polynuclear Aromatic Hydrocarbons over $ZnCl_2/CuCl$ Molten Salt Catalyst

4-1 INTRODUCTION

In the previous chapter, polynuclear aromatic hydrocarbons (anthracene, phenanthrene, pyrene, chrysene, and fluoranthene), which were supposed to be structural units of bituminous coal, were used as the model substances. The detailed product distributions and differences of the catalytic activities among some molten salts were presented and discussed. The $ZnCl_2/CuCl$ molten salt was found to be one of the superior hydrocracking catalysts for polynuclear aromatic hydrocarbons.

In the study of structural units of coal, one of the major problems is to understand the behavior of the substituents which attach to the condensed aromatic rings in the hydrocracking reaction. From this standpoint, the findings reported in the previous chapter will be applied to interprete the results obtained in the hydrocracking of alkyl-substituted polynuclear aromatic hydrocarbons, in order to clarify the effect of the alkyl substituents on the product distributions. The characteristic behavior of the alkyl groups on the starting material and the decomposition process will be described in this chapter.

4-2 EXPERIMENTAL

(1) General Procedure.

A stainless steel vessel containing 8g of feed (in the case of the unsubstituted aromatic hydrocarbon) and an equimolar amount of the catalyst ($ZnCl_2:CuCl$=60mol%:40mol%) was placed in a stainless steel (SUS 32) autoclave with a capacity of 200ml. In the hydrocracking of an alkyl-substituted or dihydro aromatic hydrocarbon, the quantity of feed used was equimolar with the unsubstituted derivative containing the same condensed rings. Hydrogen was introduced into the autoclave to achieve a pressure of 100kg/cm^2; then the autoclave was heated up to the desired temperature. This took from 60 to 70min. The reaction system was shaken in a horizontal direction (68 strokes/min) and maintained at 400°C for 3h. No attempts were made to maintain the hydrogen pressure at a constant level during the reaction. The identification and the determination of the products were carried out according to the methods described previously.

(2) Materials.

The naphthalene(Ia), 2,6-dimethylnaphthalene(Id), and fluorene(VII) were obtained from Wako Pure Chemical Industries,Ltd. The 1-methylnaphthalene(Ib), 2-methylnaphthalene(Ic), anthracene(IIa), and 9,10-dihydroanthracene(Va) were obtained from Nakarai Chemicals,Ltd. The phenanthrene(IIIa) and chrysene(IV) were obtained from Tokyo Kasei Kogyo Co.,Ltd. 9-Methylanthracene(IIb) and 9-propylanthracene(IIc) were prepared by the reaction of anthrone with methylmagnesium iodide and propylmagnesium bromide respectively.1) 2-Methylanthracene(IId) was prepared by the reduction of 2-methylanthraquinone with zinc dust in NaOH aqueous solution and toluene.2) 9,10-Dihydro-9-methylanthracene(Vb) was prepared from Va and methyl iodide by using BuLi.3) Similarly, 9,10-dihydro-9,10-dimethylanthracene(Vc) was synthesized by using Vb as the starting material. 9-Methylphenanthrene(IIIb) was prepared from 9-bromophenanthrene and methyl iodide in the presence of BuLi.4) 9-Bromophenanthrene was prepared by the addition of bromine to IIIa, followed by thermal elimination of hydrogen bromide. 9,10-Dihydro-9-methylphenanthrene (VI) was prepared by the reduction of IIIb by using Li in liquid NH_3 in the presence iron(III) chloride.4) All the purities of these compounds, determined by GC, were more than 95%. The zinc chloride and copper(I) chloride were obtained from Nakarai Chemicals,Ltd. The mixture of $ZnCl_2$ and CuCl was dried before use at 400°C for 1h in nitrogen.

(3) Classification of Products.

In order to clarify the reactivity of the starting material over the molten salt, it is necessary to know the product distribution. The products were classified for convenience into seven groups as follows: 1, C_1-C_4 gases; 2, C_5-C_7 alkanes; 3, cycloalkanes; 4, monocyclic aromatics; 5, indans, tetralins, and bicyclic aromatics; 6, dihydrobenzindenes, tricyclic aromatics, and their hydrogenated compounds; 7, coke.

4-3 RESULTS AND DISCUSSION

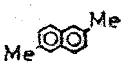
Table 4-1 shows the product distributions according to the classification method described in the experimental section. The reaction conditions were decided by considering the extent of the progress of the hydrocracking, because a high conversion is required in order to discuss the reaction process of hydrocracking based on the product distribution.

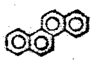
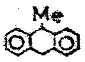
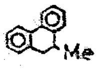
(1) Influence of the Number of Rings in the Condensed Aromatic Hydrocarbon.

Table 4-1 shows that the yield of cycloalkanes (3) increases with increasing number of rings, from the comparison of the results of naphthalene (Run 1), phenanthrene (Run 9), and chrysene (Run 11). Here, the yield of 3 in the hydrocracking of naphthalene is much lower than that in the hydrocracking of anthracene, phenanthrene, and chrysene. This finding strongly indicates that the cleavage of the C-C bonds of the central rings in highly hydrogenated polynuclear aromatic hydrocarbons containing more than three rings (ex. unsym-octahydroanthracene, unsym-octahydrophenanthrene, and so on) is one of the main decomposition pathways. Actually, the decomposition of unsym-octahydro-

Table 4-1. Distribution of Hydrocracked Products

Reaction conditions: $ZnCl_2$: CuCl = 60: 40 (mol: mol); Feed/Catalyst = 1.0 (mol/mol); initial hydrogen pressure, 100 kg/cm^2; reaction time, 3 h; reaction temperature, 400 °C.

		Run No.							
		1	2	3	4	5	6	7	8
									
	Feed	Ia	Ib	Ic	Id	IIa	IIb	IIc	IId
Products (wt %)	1	45.7	33.4	39.3	40.7	38.1	42.3	25.7	28.8
	2	3.7	6.6	6.6	7.2	7.9	7.9	10.3	10.7
	3	1.5	2.0	1.8	1.6	10.8	7.6	8.5	10.3
	4	46.4	47.7	45.3	44.8	27.7	24.3	27.6	24.6
	5	2.2	9.8	6.4	5.5	8.9	10.5	15.2	15.2
	6	—	—	—	—	2.5	5.0	11.3	10.3
	7	0.5	0.5	0.6	0.2	4.1	2.4	1.4	0.1

		Run No.							
		9	10	11	12	13	14	15	16
									
	Feed	IIIa	IIIb	IV	Va	Vb	Vc	VI	VII
Products (wt %)	1	27.7	41.4	28.2	42.0	35.9	55.6	41.7	30.6
	2	7.2	7.7	10.7	7.2	8.5	7.8	6.7	4.2
	3	7.0	6.4	17.6	8.6	8.8	3.9	6.4	6.5
	4	33.2	34.0	25.2	29.5	24.5	28.0	30.1	25.0
	5	14.6	6.0	11.0	9.1	14.5	3.0	10.0	14.3[b]
	6	5.7	3.3	4.5[a]	2.4	7.2	1.3	5.0	17.5
	7	4.6	1.2	2.7	1.2	0.6	0.4	0.1	1.9

a) containing tetracyclic compounds (1.1%). b) containing biphenyls (10.5%).

phenanthrene to 1-cyclohexyl-2-phenylethane in the hydrocracking of phenanthrene and a similar cleavage in the hydrocracking of chrysene were found and reported in the previous chapter. This finding also demonstrates that the contribution of the pathway via decalin to the decomposition process of naphthalene is minor,$^{5)}$ and that this type of catalyst is relatively inactive for the hydrogenation and hydrocracking of monocyclic aromatics. The latter seems to be desirable for obtaining a high yield of gasoline.$^{6)}$

(2) Influence of Kinds of Alkyl Groups in the Hydrocracking of Anthracenes.

Table 4-2 and 4-3 describe the composition of gases (1) and monocyclic

Table 4-2. Composition of Gases (mol%)

	Run No.															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Feed	Ia	Ib	Ic	Id	IIa	IIb	IIc	IId	IIIa	IIIb	IV	Va	Vb	Vc	VI	VII
C1[a]	33.5	22.8	23.8	22.8	20.8	29.5	20.3	26.1	20.9	21.4	21.0	17.7	40.3	50.4	34.1	23.4
C2[b]	12.8	9.9	11.4	11.5	12.2	8.9	9.3	8.4	10.5	7.8	8.5	10.8	7.8	6.9	9.0	12.7
C3[c]	25.6	30.8	31.4	28.6	29.3	27.6	45.7	22.0	31.9	34.6	26.8	32.2	22.3	19.6	26.8	33.9
C4[d]	28.1	36.5	33.4	37.1	37.7	34.0	24.7	43.5	36.7	36.2	43.7	39.2	29.6	23.1	30.1	30.1

a) Methane. b) Ethane. c) Propane. d) Butanes and butenes.

Table 4-3. Composition of Monocyclic Aromatics (mol%)

	Run No.															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Feed	Ia	Ib	Ic	Id	IIa	IIb	IIc	IId	IIIa	IIIb	IV	Va	Vb	Vc	VI	VII
A[a]	68.9	25.7	25.9	7.9	41.7	27.9	41.4	19.9	38.4	23.0	39.1	39.1	26.3	19.0	22.1	47.9
B[b]	16.5	34.4	35.8	33.7	26.9	27.8	28.8	31.8	23.4	31.0	26.3	24.4	27.1	25.1	29.2	26.8
C[c]	11.3	28.3	27.9	31.3	17.5	24.0	16.3	22.6	23.3	28.6	22.5	24.7	29.9	32.5	29.5	19.3
D[d]	1.9	9.0	8.5	20.0	7.7	13.7	8.7	13.7	8.2	11.2	7.3	7.0	10.8	17.5	13.9	4.8
E[e]	1.4	2.6	1.9	7.1	6.2	6.6	4.8	12.0	6.7	6.2	4.8	4.8	6.0	5.9	5.3	1.1
R[f]	4.18	0.75	0.72	0.23	1.55	1.00	1.44	0.63	1.64	0.74	1.49	1.60	0.97	0.76	0.76	1.79

a) Benzene. b) Toluene c) Ethylbenzene and xylenes (C_2 alkylbenzenes).
d) C_3 alkylbenzenes. e) Alkylbenzenes containing more than C_4.
f) R=benzene/toluene (mol/mol).

aromatics (4) respectively. The behavior of the alkyl group can be deduced by using these results, because the difference in the composition of 1 or 4 between the alkyl-substituted polynuclear aromatic hydrocarbon and the corresponding unsubstituted compound is apparent. First the results for anthracene derivatives will be discussed and the reactivity of IIb will be compared with that of IIc. Two experiments (Runs 6 and 7) were carried out to investigate the difference of the composition of the products in accordance with the change in the alkyl group. The relative content of methane in Run 6 is higher than that in Run 5. Similarly the relative content of propane in Run 7 is quite a bit higher than that in Run 5. These findings show that the alkyl group is eliminated in the course of hydrocracking. In the case of methyl-substituted polynuclear aromatics, the ratio of benzene to toluene (R) is supposed to indicate the extent of demethylation, because the value may increase with increasing demethylation according to the main reaction scheme, as shown later (cf.Fig. 4-1), and this ratio was used as a convenient measure of demethylation. The comparison of R in Run 6 with R in Run 5 shows that the methyl group of IIb is conserved in monocyclic aromatics in the course of hydrocracking. The ratio of the yield of unsubstituted tricyclic compounds to that of alkylated tricyclic compounds was 8.9 in the case of IIc and 2.3 in the case of IIb. In addition, the composition of monocyclic aromatics in Run 7 was very similar to that in Run 5. All of these findings indicate that the propyl group is dealkylated more easily than the methyl group. Similar phnomena were observed in the hydrocracking of alkylbenzenes in the presence of acidic catalysts.7) These findings may be explained by considering that propylanthracene possesses the possibility of isomerization to isopropylanthracene and that the secondary alkyl group can be dealkylated in preference to the primary alkyl group.7,8) The similarity between IIa and IIc in the composition of monocyclic aromatics would demonstrate that the propyl group of IIc is mainly dealkylated in the initial decomposition stage. On the other hand, the decomposition process of the marginal hydrogenated rings prior to dealkylation is also considered to be of importance in the case of IIb.

(3) Influence of Positions of Alkyl Groups and Types of Condensed Rings.

Since the presence of methyl group remarkably influenced the decomposition of the polynuclear aromatics, the methyl derivatives were used for the following experiments. The experiments of IIb and IId were carried out to clarify the effect of the position of methyl group attached to the anthracene skeleton on the composition of the decomposed products. The value of R in IId is lower than that in IIb; this finding suggests that the methyl group of IId is well conserved in monocyclic aromatics in comparison with that of IIb. This result is interpreted by the idea that the demethylation prior to the hydrocracking of the condensed ring has a minor contribution to the reaction process in the hydrocracking of IId, that is, the methyl group of IIb is eliminated more easily than that of IId. The experiments of IIb and IIIb were carried out to clarify the difference of the type of condensed rings. The ease of demethylation in the initial decomposition process differs in these two cases. The methyl group of IIIb is conserved in monocyclic aromatics much more frequently than that of IIb. It is noteworthy that the composition of monocyclic aromatics of IV is fairly similar to that of IIIa. The effect of the presence of the methyl group on the composition of monocyclic aromatics (Run 10) is observed more dramatically than that of the increase of the number of the aromatic rings (Run 11).

(4) Hydrocracking of Naphthalenes.

It is noteworthy that a remarkable difference in the R values was observed in the hydrocracking of naphthalene derivatives (Runs 1-3). This finding suggests that the unsubstituted ring is more easily hydrogenated than the methylated ring. This fact is the basis for asserting that the alkyl groups on the polynuclear aromatic hydrocarbons influence the composition of monocyclic aromatics in this hydrocracking. The effect of the position of the methyl group on the composition of monocyclic aromatics was hardly observed in the case of Ib and Ic (Runs 2 and 3). The experiment of Id (Run 4) seems to be most suitable for investigating the demethylation. If Id never undergoes the demethylation , the yield of benzene should become zero. The presence of a little quantity of benzene demonstrates the occurence of demethylation; however, the contribution of the demethylation in the initial stage to the composition of monocyclic aromatics seems rather insignificant.

(5) Hydrocracking of Dihydro Tricyclic Aromatics.

The hydrocrcking of Va is of importance for clarifying the decomposition process of IIa.[9-11] If the central methylene bridge of Va is ruptured, the yield of monocyclic aromatics should increase remarkably compared with IIa. However, the product distributions of these two hydrocracking reactions are similar: Va seems to undergo dehydrogenation, followed by the decomposition process, in a way similar to IIa. The experiments of Vb and Vc were carried out in anticipation of the specific reaction caused by introducing the methyl group(s) to the central carbon atom(s) of 9,10-dihydroanthracene. The product distribution of Vb (Run 13) is successfully explained by considering that the dehydrogenation and demethylation occurred in the initial stage; that is, Vb was mainly decomposed via IIa or IIb. Vc is also considered to be decomposed in a manner similar to Vb, and so the opening of the central ring of this type of compound is considered to be small in this hydrocracking reaction. Fig.4-1 shows the main decomposition scheme of 9,10-dihydroanthracene derivatives. The ease of dealkylation of the butyl group compared with the methyl group is considered to govern this decomposition process. If the C_{8a}-C_9 bond of VI is fairly well cleaved, the yield of biphenyl derivatives in the hydrocracking of VI should be higher than that in the hydrocracking of IIIb. However, no such increase of the yield of biphenyl derivatives could be observed, and so VI seems to undergo demethylation and dehydrogenation in the initial decomposition process. On the other hand, the pathway to the biphenyl derivatives becomes very important in the case of VII, because VII has no pathway of dehydrogenation to the stable aromatic compounds. In this case, the lowering of the reactivity was observed.

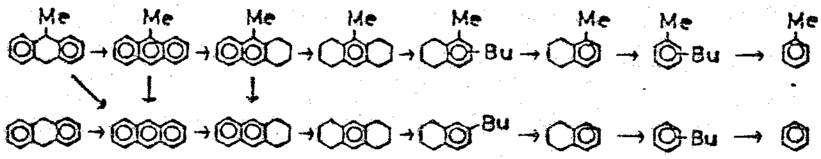


Fig. 4-1. Main Reaction Scheme of Dihydroanthracene Derivatives

4-4 CONCLUSION

The hydrocracking of alkyl-substituted polynuclear aromatic hydrocarbons was carried out to clarify the decomposition scheme and the behavior of the alkyl group. The findings are outlined as follows: 1) The decomposition route via highly hydrogenated compounds becomes important with increasing numbers of rings of the polynuclear aromatics. 2) The alkyl group substituted on the polynuclear aromatic hydrocarbon is not completely dealkylated in the initial stage and remains in the products as monocyclic aromatics. The extent of dealkylation depends on the properties (that is, kinds and positions of alkyl groups, and types of condensed rings) of the starting materials. 3) In the hydrocracking of 9,10-dihydroanthracene, the dehydrogenation occurs in preference to the opening of the central ring; in the hydrocracking of the methylated 9,10-dihydroanthracenes and 9,10-dihydrophenanthrene, the dehydrogenation and demethylation take place in preference to the opening of the central ring; but in the hydrocracking of fluorene, the pathway to the biphenyls becomes important. These findings are expected to be useful for understanding the hydrocracked mechanism and the composition of the resulting products of coal.

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CHAPTER 5

The Hydrocracking of Solvent Refined Coals over Molten Salt Catalysts

5-1 INTRODUCTION

Although the detailed structure of coal has never been clarified, some structural analyses suggest that coal is the natural polymer possessing several structural units consisted of mainly condensed rings. Consequently, in order to obtain liquid fuels from coal, it is necessary to decompose the condensed rings in addition to the scission of the bond between the structural units. From this standpoint, the hydrocracking of model substances of coal (that is, a heavy anthracene oil and polynuclear aromatic hydrocarbons) over molten salts was investigated and $ZnCl_2/CuCl$ molten salt was found to be one of the superior hydrocracking catalysts for the coal related substances based on the detailed product analyses. In this chapter, this catalyst system will be applied to the hydrocracking of solvent refined coals (SRC), which is considered to be representative of structural units of coal, and the catalytic action of this catalyst system for SRC will be examined in comparison with $ZnCl_2$.

5-2 EXPERIMENTAL

The NMR spectra were recorded on a Jeol JNM-PS-100 spectrometer, using tetramethylsilane as the internal standard. $CDCl_3$ was used as the solvent for all the substances. 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 20eV connected with a Hatachi M 5201 apparatus using a 3m x 3mm column of 5% Silicone OV-1 on Uniport KS. The average molecular weights were determined with a Hitachi-

Perkin Elmer 115 vapour pressure osmometer in chloroform and bibenzyl was used as the calibration standard. The zinc chloride and copper(1) chloride were obtained from Nakarai Chemicals,Ltd.

(1) Preparation of SRC.

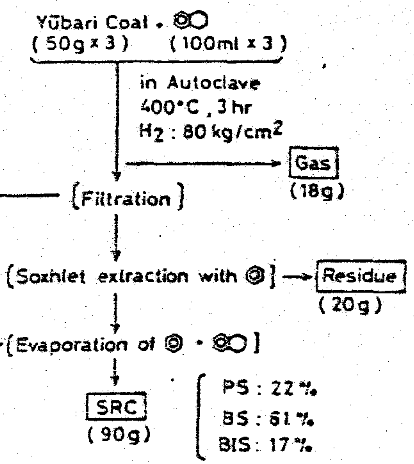
Experiments were carried out in a 500ml SUS 32 autoclave, 50g of Yūbari coal (-200mesh) and 100ml of tetralin were charged and hydrogen was pressured up to 80kg/cm². The rate of the temperature rise was controlled to about 3°C/min up to 400°C, after which the temperature was held for 3h. The autoclave was shaken in a horizontal direction (70 strokes/min). No attempts were made to maintain the hydrogen pressure at a constant level during the reaction. After the system had been cooled to room temperature, gases were collected in a gas holder and analyzed by GLC (60-80mesh Silica gel column, 3m x 3mm, TCD, 120°C, N_2 Carrier). The product was filtered and the residue was extracted with benzene by Soxhlet extractor. The above procedure was repeated 3 times. The benzene and tetralin were removed from the combined mixture of filtrates and extracted solutions. The yield of Yūbari SRC was 90g. In the case of Tempoku coal, the reaction time was 30min and the autoclave experiment was repeated 4 times. The yield of Tempoku SRC was 70g. All the properties of coals and their SRC are shown in Table 5-1.

Table 5-1. Properties of Coal and SRC

	Ultimate analyses a)				Structural parameters b)			
	H	C	N	O c)	fa	σ	Hau/Ca	Mw d)
Yūbari Coal	6.0	86.1	2.1	5.8	—	—	—	—
Yūbari SRC	6.4	88.9	2.2	2.6	0.73	0.28	0.63	506
Tempoku Coal	5.4	69.8	1.9	22.9	—	—	—	—
Tempoku SRC	6.3	87.2	1.7	4.8	0.76	0.26	0.69	340

a) d.a.f. b) by Brown-Ladner's method c) difference d) $CHCl_3$

Preparation of Yūbari SRC



(2) Hydrocracking of SRC.

A stainless steel vessel containing 8g of SRC and the catalyst was placed in a SUS 32 autoclave with a capacity of 200ml. The air in the autoclave was replaced by hydrogen, and then the system was filled with hydrogen to 100 kg/cm^2; then the autoclave was heated up to the desired temperature. The time taken to reach the stage was from 60 to 70min. The reaction system shaken in a horizontal direction (68 strokes/min) was maintained at the reaction temperature for 3h. No attempts were made to maintain the hydrogen pressure at a constant level during the reaction. After the system had been cooled to room temperature, gases were collected in a gas holder and analyzed by GC. The liquid and solid products were extracted with pentane by Soxhlet extractor and the residues subjected to benzene extraction. Moreover, the pentane extracts were separated into two fractions (PSL and PSH) by means of vacuum distillation (-190°C/3mmHg). The lighter fraction (PSL) was analyzed by GC (4.5m x 3mm packed with 20% SE-30 on Uniport B 60-80mesh, programmed from 30 to 270°C, 5°C/min, TCD, H_2 Carrier).

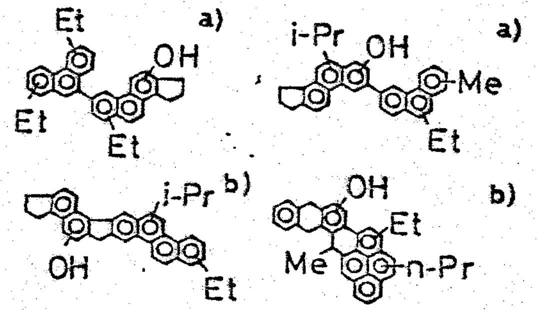
5-3 RESULTS AND DISCUSSION

(1) Average structure of SRC.

SRC consists of large numbers of compounds possessing the different molecular weights, moreover the constituents cannot be determined. However, as these compounds are supposed to consist of similar type compounds, the concept of the average structure has been employed for a variety of structural analyses. In this investigation, the average structure of SRC was estimated according to the CAMSC method proposed by Oka et al.1) This CAMSC method attempts to represent the average structure as a combination of aromatic and aliphatic groups, in accordance with the input data represented as integral numbers based on experimental data from elemental, NMR, and molecular weight analyses. Oxgen atoms were considered as a phenolic OH, as an ether, or as a carbonyl group, on the other hand, sulfur and nitrogen atoms were not considered. The determination of average structures has been carried out by the computor program prepared according to the flow chart and the classification method by Oka et al. The results of Yūbari SRC and Tempoku SRC are shown in Figs. 5-1 and 5-2 respectively. It is supposed to be unreasonable that the average structure is represented by a single structure. It is preferable to divide the average structures obtained by the CAMSC method broadly into two types, that is, the type containing the direct bond between two aromatic rings (a) and the type containing a large ring structure (b).

(2) Hydrocracking of SRC.

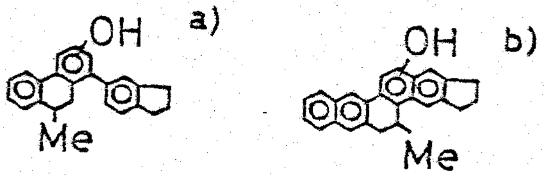
The SRC, which received thermal scission of the bonds between structural units and stabilization by hydrogen transfer from tetralin, is the primary hydrocracked product of coal and is regarded as representative of the structural units of coal. The difference of the structural parameters calculated by using



Average structure of Yūbari SRC by CAMSC

Experimental result: Hα=9.4, Ho=10.5, Hal=19.9, Har=12.2, Car=28.0, Cal=9.4,(OH=0.82).
Input data for CAMSC: Hα=9, Ho=11, Hal=20, Har=12, Car=28, Cal=9,(OH=1).

Fig. 5-1. Average Structure of Yubari SRC



Average structure of Tempoku SRC by CAMSC

Experimental result: Hα=6.9, Ho=5.0, Hal=11.9, Har=9.6, Car=19.0, Cal=5.7,(OH=0.79).
Input data for CAMSC: a) Hα=7, Ho=5, Hal=12, Har=10, Car=18, Cal=6,(OH=1). b) Car=20.

Fig. 5-2. Average Structure of Tempoku SRC

Brown-Ladner's method$^{2)}$ and average molecular weight between Yūbari SRC and Tempoku SRC suggests that the structure of the SRC considerably reflects the original structure of coal. On the other hand, as SRC is molten at this reaction temperature and becomes homogeneous liquid, the catalytic action of the molten salts for SRC is expected to be similar to that for polynuclear aromatic hydrocarbons (PAH). From these standpoints, SRC was selected as a kind of model substances of coal.

Table 5-2. Hydrocracking of Yūbari SRC[a)]

		Run No.								
		1	2	3	4	5	6	7	8	9[b)]
Catalyst		ZnCl$_2$	ZnCl$_2$/CuCl		ZnCl$_2$	ZnCl$_2$/CuCl	ZnCl$_2$	ZnCl$_2$/CuCl	ZnCl$_2$/CuCl	ZnCl$_2$/CuCl
(mol:mol)			(60:40)			(60:40)		(90:10)	(60:40)	(60:40)
Catalyst/feed (wt/wt)		0.1	0.1		0.1	0.1	1	1	1	1
Reaction Temp. (°C)		350	350	400	400	400	400	400	400	400
Products (wt%)	Gas	2	3	9	13	14	25	29	36	40
	PSL	2	2	7	16	19	32	32	24	34
	PSH	25	34	19	39	41	28	22	13	8
	BS	48	42	61	17	14	1	1	1	1

a) Yūbari SRC consists of 22% of PS, 61% of BS, and 17% of BIS. b) Tempoku SRC

Reaction conditions: initial hydrogen pressure, 100kg/cm^2; reaction time, 3h.

The results of the hydrocracking of SRC are shown in Table 5-2. The products were classified into Gas, PSL, PSH, and BS. The GC charts of the hydrocracked products of Yūbari SRC are shown in Figs.5-3 and 5-4. The products listed in Figs.5-3 and 5-4 were identified by means of GC-MS and by reference to the GC charts of the hydrocracked products of PAH. The structural parameters, the average molecular weight, and nitrogen content of the hydrocracked products of Yūbari SRC are shown in Table 5-3. Then, the catalytic action of molten salts will be discussed based on the product distribution shown in Table 5-2 and the properties shown in Table 5-3.

The reaction conditions of Runs 6-8 were established by considering the case of PAH. As the yield of gas increases with increasing the content of CuCl, the cracking ability of the catalyst is considered to be increased by the

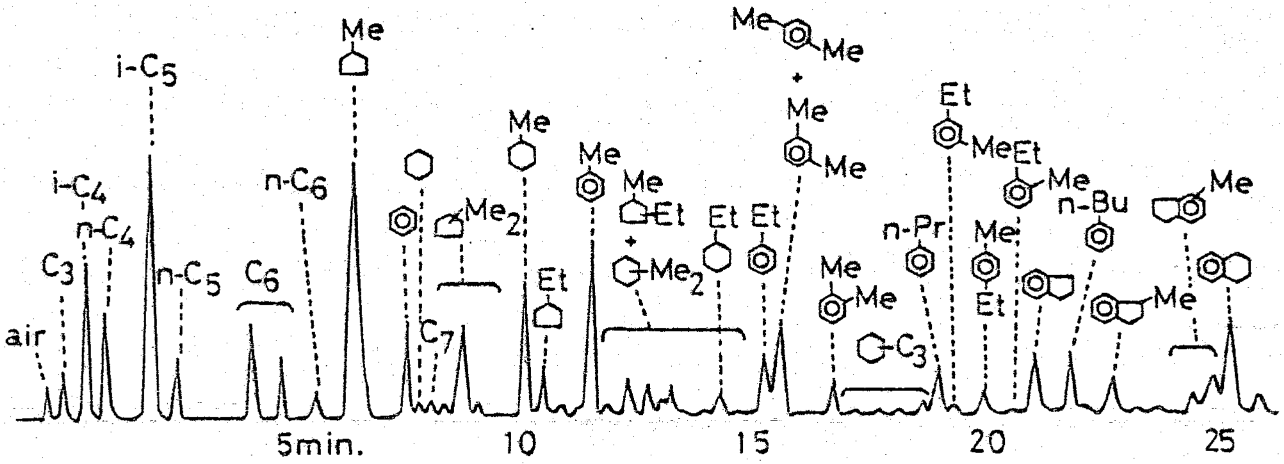


Fig. 5-3. Gas Chromatogram of Hydrocracked Products of Yūbari SRC (Part I)

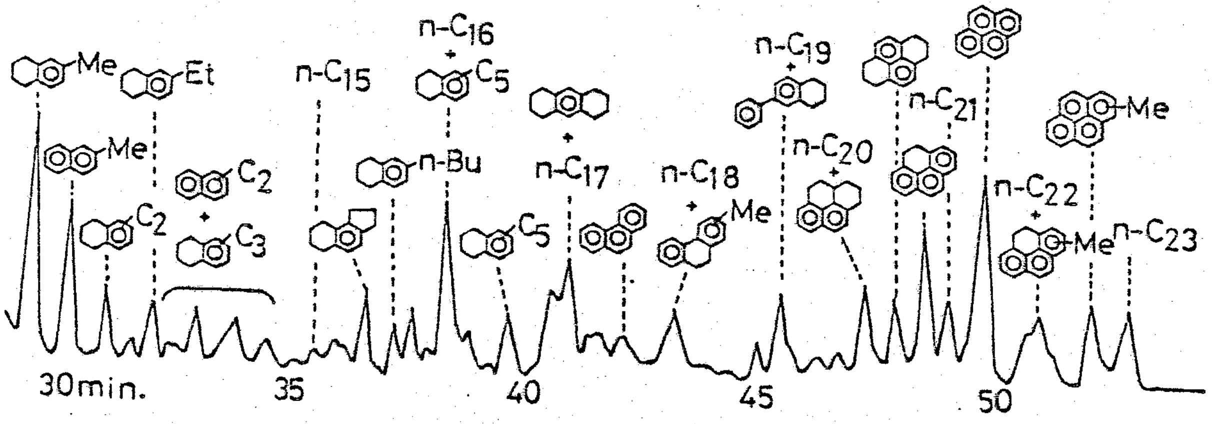


Fig. 5-4. Gas Chromatogram of Hydrocracked Products of Yūbari SRC (Part II)

Table 5-3. Properties of Hydrocracked Products of Yūbari SRC

Sample	fa	Hau/Ca	Mw	N(%)
SRC-PS	0.61	0.78	284	2.12
3-PSH	0.59	0.79	288	1.66
4-PSH	0.57	0.79	285	0.57
5-PSH	0.57	0.79	283	0.64
6-PSH	0.61	0.71	273	—
7-PSH	0.63	0.73	257	—
8-PSH	0.60	0.70	268	—
SRC-PS	0.76	0.63	511	2.40
3-BS	0.75	0.57	487	2.29
4-BS	0.74	0.58	376	1.05
5-BS	0.75	0.57	403	0.98

addition of CuCl; but the undesirable recombination of fragments also seems to be accelerated.3) Accordingly, more mild conditions than the conditions in Runs 6-8 are considered to be demanded for the hydrocracking of SRC. The quantity of catalyst was decreased in Runs 3-5, and the reaction temperature was lowered in Runs 1 and 2.

The average molecular weights and the structural parameters of PSH in Runs 4 and 5 are similar to them in Run 3. On the other hand, the average molecular weights of BS in Runs 4 and 5 are less than that in Runs 3. By comparison of the product distributions in Runs 3-5, the increase of the amounts of Gas, PSL, and PSH, the decrease of the amounts of BS, and the lowering of the average molecular weight of BS strongly demonstrate that these molten salts are remarkably effective for the hydrocracking of Yūbari SRC. In addition, denitrogenation was found to be acceleralated by the catalytic action of the molten salts.

In the hydrocracking of PAH at 400°C the catalytic activity of $ZnCl_2$/CuCl molten salt had been found to be greatly higher than $ZnCl_2$ molten salt. But in the hydrocracking of SRC at 400°C over these molten salt catalysts, the difference of the catalytic activity was not so remarkable. In comparison with PAH examined in chapter 3, SRC possesses higher average molecular weight and hetero atoms. These factors are supposed to reduce the difference of the catalytic activity of these two catalyst systems. Morita et al.[5) had reported that the hydroxyl group attaching to the aromatic ring facilitates the hydrocracking of of the aromatic ring. The results of the hydrocracking of naphthalene and β-naphthol over the molten salts shown in Table 5-4 supported this consideration, and the hydroxyl group[6) existing in SRC is supposed to facilitate the hydrocracking of SRC. Accordingly, hydroxyl groups are anticipated to be important in reducing the difference of the catalytic activity of these two catalysts.

At 350°C (Runs 1 and 2), the difference of these two catalysts was observed in the yield of PSH and BS.

Table 5-4. Influence of OH Substituent on the Product Distribution

Feed		naphthalene		β-naphthol	
Catalyst		$ZnCl_2$	$ZnCl_2$/$CuCl_2$	$ZnCl_2$	$ZnCl_2$/$CuCl_2$
(mol:mol)			(60:40)		(60:40)
Products (wt%)	C_1-C_4 gases	3.4	45.7	26.3	56.0
	C_5-C_7 alkanes	-	3.7	1.1	2.9
	cycloalkanes	0.1	1.5	3.2	3.1
	monocyclic aromatics	2.0	46.4	18.7	33.7
	indans and tetralins	16.0	1.7	31.2	3.0
	naphthalene	77.9	0.5	9.3	0.7
	higher boiling products	0.7	-	10.3	0.6

Reaction conditions: initial hydrogen pressure, 100kg/cm^2; reaction time, 3h; reaction temperature, 400°C. Catalyst/Feed=1(mol/mol).

In the hydrocracking of PAH, it was clarified that the product distribution is dependent upon the original structure and the methyl groups in the feed remarkably effect on compositions of monocyclic aromatics and of gases. Based on the results obtained in the hydrocracking of SRC under the conditions similar to the hydrocracking of PAH, the structure of SRC will be discussed.

Table 5-5. Influence of Ring Size on the Product Distribution

Substances used for hydrocracking	cycloalkanes/monocyclic aromatics[a]
bicyclic compounds[b]	0.03-0.04
tricyclic compounds[c]	0.14-0.42
chrysene	0.70
Tempoku SRC	0.82
Yūbari SRC	1.11

a)wt/wt b) naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 2,6-dimethylnaphthalene c) anthracene, 9-propylanthracene, 2-methylanthracene, 9-methylanthracene, 9,10-dihydroanthracene, 9,10-dihydro-9-methylanthracene, 9,10-dihydro-9,10-dimethylanthracene, phenanthrene, 9-methylphenanthrene, 9,10-dihydro-9-methylphenanthrene, fluorene.

Monocyclic aromatics are relatively stable in these reaction conditions. On the other hand, cycloalkanes are mainly formed via highly hydrogenated compounds (for example, unsym-octahydrophenanthrene in the hydrocracking of phenanthrene), and so the yield of cycloalkanes is expected to increase with increasing the size of the original ring structure. The ratio of the amounts of cycloalkanes to those of monocyclic aromatics in the hydrocracked products shown in Table 5-5 is considered to be a measure of the size of the ring structure. If SRC consisted of alkyl-substituted PAH, they are supposed to have larger ring structure than chrysene in average. This finding suggests that the type containing a large ring structure (b) is more important than that containing the direct bond between two aromatic rings (a) in the average structures shown in Figs. 5-1 and 5-2 between these two SRC.

Table 5-6. Composition of Monocyclic Aromatics (mol%)

	Yubari SRC	Tempoku SRC
A	14.2	27.0
B	25.0	27.7
C	28.7	26.8
D	20.2	12.3
E	12.0	6.2
R	0.57	0.97

A) benzene B) toluene C) ethylbenzene and xylenes(C_2 alkylbenzenes) D) C_3 alkylbenzenes E) alkyl benzenes containing more than C_4.
R=benzene/toluene(mol/mol)

Table 5-7. Composition of Gases (mol%)

	Yubari SRC	Tempoku SRC
C1	40.0	39.1
C2	17.7	17.7
C3	19.3	20.7
C4	22.9	22.5

C1) methane C2) ethane C3) propane
C4) butanes and butenes

In the hydrocracking of alkyl-substituted PAH, the behavior of the alkyl group attached to the condensed ring had been found to be different. The methyl group was not completely dealkylated in the initial stage and remained in the products as monocyclic aromatics; the extent of dealkylation had been found to be dependent upon the type of starting materials. Table 5-6 suggests that Yūbari SRC possesses a lot of alkyl groups as the substituents in comparison with Tempoku SRC. On the other hand, Table 5-7 indicates that the extent of dealkylation is similar to that of Tempoku SRC. These results seem to support the idea that average structures shown in Figs. 5-1 and 5-2 considerably reflect the characteristics of the real structure of these two SRC.

5-4 REFERENCES

1) M.Oka, H.-C.Chang, and G.R.Gavalas, Fuel, 56, 3 (1977).

2) J.K.Brown and W.R.Ladner, Fuel, 39, 87 (1960).

3) In the isomerization of cyclohexene at 400°C over the molten salts,[4] the yield of isomerized products was found to be remarkably dependent upon the composition between $ZnCl_2$ and CuCl. The catalytic activity for the isomerization displayed the maximum in a ratio of 2:1 ($ZnCl_2$:CuCl).

4) Y.Nakatsuji, K.Shigeta, M.Nomura, and S.Kikkawa, unpublished data.

5) M.Morita and K.Hirosawa, Nippon Kagaku Kaishi, 1975, 1555.

6) C.W.Dewalt,Jr. and R.A.Glenn, Anal.Chem., 24, 1789 (1952).
Hydroxyl groups were determined by acetylation using acetic anhydride. The values are shown in experimental result of Figs. 5-1 and 5-2.

CHAPTER 6

The Hydrocracking of Yūbari Coal Supported with Metal Halides

6-1 INTRODUCTION

The $ZnCl_2/CuCl$ molten salt was found to be one of the superior catalysts for several model substances of coal in comparison with $ZnCl_2$ alone as previously stated. In this chapter, this catalyst system will be applied to the hydrocracking of Yūbari coal which is the one of the typical Japanese bituminous coals.

6-2 EXPERIMENTAL

Zinc halide ($ZnCl_2$ or ZnI_2) was supported on Yūbari coal (-32mesh) through the impregnation of its methanol solution, then the slurry was dried by evaporating the methanol at 105°C, 5mmHg for 30min. In the case of ZnX_2/CuX (X=Cl,I) supported coal, coal was added to the methanol solution dispersed with CuX, and then the methanol was removed under the above conditions. $ZnCl_2$, CuCl, and CuI were obtained from Nakarai Chemicals,Ltd. ZnI_2 was obtained from Mitsuwa Chemicals Co.,Ltd.

A stainless steel vessel containing the coal (10g) treated with metal halide was placed in an autoclave (Hastelloy F) with a capacity of 200ml. The system was flushed and filled with hydrogen to $100kg/cm^2$ and heated up to 400°C; the time taken to reach 400°C was 60min. The reaction system was shaken in horizontal direction (68 strokes/min). After the reaction, the system was cooled to room temperature, and gaseous products were collected in a gas holder and analyzed by GLC. The liquid and solid products in the autoclave were scraped out with pentane and extracted in a Soxhlet apparatus with pentane and then with benzene for 20h, respectively. The solvent of the extracted solution was removed in vacuo. The structural parameters of hydrocracked products were calculated using Brown-Ladner's method$^{1)}$ on the basis of the data of ^1H NMR and elemental analysis. The apparatus used for analytical methods were described in detail previously.

6-3 RESULTS AND DISCUSSION

The catalytic action of molten salts will be discussed based on the product distribution shown in Table 6-1 and the properties shown in Table 6-2.

Table 6-1. Hydrocracking of Yūbari Coal

		Run No.			
		1	2	3	4
Catalyst		$ZnCl_2$	$ZnCl_2$/ $CuCl_2$	ZnI_2	ZnI_2/ CuI_2
Products (wt%)	Gas	13	15	14	23
	PS	36	43	50	57
	BS	41	38	20	15

H_2: 100kg/cm^2; 400°C; 3h; ZnX_2/CuX=5(mol/mol); ZnI_2: 5wt%; $ZnCl_2$: equimolar to ZnI_2.

Table 6-2. Properties of Hydrocracked Products of Yūbari Coal

Sample	fa	Hau/Ca	Mw
1-PS	0.62	0.68	265
2-PS	0.54	0.68	250
3-PS	0.55	0.75	280
4-PS	0.55	0.78	250
1-BS	0.71	0.58	625
2-BS	0.71	0.62	585
3-BS	0.70	0.57	625
4-BS	0.69	0.60	585

By comparison of the product distribution and the properties in Runs 1 and 2, the increase of the amounts of Gas, PS, the decrease of BS, and the lowering of the average molecular weight of PS and BS strongly demonstrate that $ZnCl_2/CuCl$ molten salt is superior to $ZnCl_2$ molten salt. In addition, it is noteworthy that similar trend was found in the case of iodides.

These reaction conditions were established in connection with the hydrocracking of polynuclear aromatic hydrocarbons (chapters 3 and 4), and so the characteristics of this catalyst system should be clarified by changing the reaction conditions (hydrogen pressure, reaction temperature, reaction time, and so on).

6-4 REFERENCES

1) J.K.Brown and W.R.Ladner, Fuel, 39, 87 (1960).

CHAPTER 7

Conclusion

This thesis mainly describes the difference of catalytic activities between $ZnCl_2/CuCl$ molten salt and $ZnCl_2$ molten salt in the hydrocracking of coal related substances (a heavy anthracene oil, polynuclear aromatic hydrocarbons, solvent refined coals, and Yūbari coal). The results obtained in the course of this investigation are summarized as follows.

1) $ZnCl_2/CuCl$ molten salt was found to display an excellent catalytic activity for the hydrocracking of polynuclear aromatic hydrocarbons in comparison with $ZnCl_2$ molten salt based on the detailed product analysis mainly using GC-MS. This catalyst system is considered to act as a molten dual-functional catalyst.

2) The findings with regard to the reaction routes over $ZnCl_2/CuCl$ molten salt may be outlined as follows: i) the isomerization between sym-octahydrophenanthrene and sym-octahydroanthracene in the hydrocracking of phenanthrene and anthracene, and a similar isomerization in the hydrocracking of chrysene; ii) the decomposition of unsym-octahydrophenanthrene to 1-cyclohexyl-2-phenylethane in the hydrocracking of phenanthrene and a similar cleavage in the hydrocracking of chrysene; iii) a decomposition pathway leading to biphenyls in the hydrocracking of fluoranthene. cata-Condensed polynulear aromatic hydrocarbon (anthracene, phenanthrene, and chrysene) was hydrocracked more efficiently than peri-condensed polynuclear aromatic hydrocarbon (pyrene).

3) This is the first investigation with regard to the behavior of the alkyl groups attaching to polynuclear aromatic hydrocarbons over molten salts. The

findings are outlined as follows. i) The decomposition route via highly hydrogenated compounds becomes important with increasing numbers of rings of the polynuclear aromatics. ii) The alkyl group substituted on the polynuclear aromatic hydrocarbon is not completely dealkylated in the initial stage and remains in the products as monocyclic aromatics. The extent of dealkylation depends on the properties of the starting materials. iii) In the hydrocracking of methylated 9,10-dihydroanthracenes and 9,10-dihydrophenanthrene, the dehydrogenation and demethylation take place in preference to the opening of the central ring; but in the hydrocracking of fluorene, the pathway to the biphenyls becomes important.

4) The relation between the average structure of SRC and the reactivity of SRC over molten salts was discussed based on the results obtained in the study using a variety of polynuclear aromatic hydrocarbons.

5) As SRC or coal possesses its own properties, the establishment of the reaction conditions in the hydrocracking must be changed according to circumstances, but $ZnCl_2/CuCl$ molten salt was found to be one of the superior catalysts for SRC and coal as well as for polynuclear aromatic hydrocarbons.

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