Yūbari Coal Depolymerization and Catalysis of ZnCl_2 -containing Melt for Hydrocracking of the Coal Extract

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In the depolymerization of Yūbari coal in the presence of tetralin, reaction time did not alter the average molecular weight of the coal extract but it effected deoxygenation and hydrogenation in which its nitrogen content remained constant. These effects are explained by referring to the average structure's change of two coal extracts. The coal extract from the depolymerization was hydrocracked over ZnCl_2 or over ZnCl_2 -CuCl melt at 400°C for 3 hr with an initial hydrogen pressure of 100 kg/cm². Analysis of PSH (higher boiling portion of pentane soluble) and of BS (benzene soluble) revealed that ZnCl_2 -CuCl was superior to ZnCl_2 in removing the heteroatoms. The effectiveness of ZnCl_2 -containing melts for denitrogenation of coal and coal related materials was discussed on the basis of hydrocracking of quinoline over ZnCl_2 and over quinoline- ZnCl_2 complex. The close similarity of these products strongly suggests that denitrogenation of the basic fraction of the coal extract proceeds via the complex formation of nitrogen atoms with ZnCl_2 .

1. Introduction

In the course of the studies^{1)~3)} on hydroliquefaction of coal and coal related materials, the authors found that the use of large amounts of ZnCl_2 -containing molten salt was very effective in eliminating the nitrogen atoms thoroughly from the oil produced and for getting lighter oil fractions in high yields.

In this study, the activities of ZnCl_2 and ZnCl_2 -CuCl melt catalysts for hydrocracking of the extract obtained from 30-min depolymerization of Yūbari coal were examined. The coal extract was prepared⁴⁾ in the presence of tetralin at 400°C. The effect of reaction time on the structure of the extract was studied in order to get a better understanding of the reactions involved in depolymerization of the coal.

Characteristic features of ZnCl_2 -containing melt for removing nitrogen atoms strongly suggest the presence of an appreciable extent of interaction between nitrogen-containing compounds and ZnCl_2 . The authors employed quinoline and γ -picoline as models of nitrogen-containing compounds. They prepared complexes of the model compounds and ZnCl_2 ^{5),6)} and hydrocracked them to study catalysis

of ZnCl_2 -containing melts in the hydrocracking reaction.

2. Experimental

2.1 Reagents: Zinc chloride and cuprous chloride (Guaranteed reagent grade) were obtained from Nakarai Chemicals, Ltd. The salts were melted in a Pyrex tube at 400°C and dried by bubbling a N_2 stream through the melt for 3 hr. Each molten salt was poured into a quartz glass pot under N_2 atmosphere; then a desired amount of the salt was sealed in a test tube under vacuum. Quinoline, γ -picoline (Nakarai Chemicals Ltd.), tetralin (Wako Pure Chemicals Co. Ltd.), and other organic solvents were purified by conventional procedures.

2.2 Preparation of the coal extract: Yūbari coal was ground to -200 mesh, dried in an oven at 105—110°C, and stored in an air-tight container. The dried coal contained 4.6% ash. The ultimate analysis (daf basis) was as follows: C% 86.1; H% 6.0; N% 2.1; O% 5.8 (by difference). The dried coal (50 g) and tetralin (100 ml) were charged to a 500 ml-autoclave and raised the pressure of H_2 to 80 kg/cm². The mixture was then heated to 400°C at a rate of about 3 °C/min, and it was held at this temperature for 30 min (or 3 hr). Shaking (68 strokes/min) was started when the temperature had reached 200°C.

The solvent extraction scheme, together with the material balance (Figures in parentheses indicate the sum of three runs), is shown in **Fig. 1**.

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Table 1 Analytical Data of Coal Extracts

Duration of Reaction	Micro-analysis ^{a)}				H/C	Structural Parameter ^{b)}			M. W.
	C%	H%	N%	O% ^{c)}		f _a	H _{aru} /C _{ar}	σ	
30 min	88.4	6.1	2.2	3.3 (3.1) ^{d)}	0.83	0.74	0.59	0.27	498
3 hr	88.9	6.4	2.2	2.6 (2.6)	0.86	0.73	0.63	0.28	506

^{a)} wt% based on d. a. f. coal. ^{b)} Brown-Ladner equation. ^{c)} difference. ^{d)} phenolic OH.

Fig. 1 Preparation of Yūbari Coal Extract

2.3 Hydrocracking of the coal extract and nitrogen-containing model compounds over molten salt catalyst:

The coal extract (or a model compound, 10 g) and the melt (10 g) were charged to a 200 ml-autoclave, which was then purged 3 times with hydrogen. The autoclave was heated up to 400°C and was held at the temperature for a predetermined length of time.

Details of products treatment were described elsewhere.⁷⁾ The pentane-soluble portion was separated into two fractions by vacuum distillation: PSL, the fraction distilled at temperatures up to 190°C under 3 mmHg and PSH, the residue. BS means a benzene-soluble and pentane-insoluble fraction.

2.4 Separation of basic fraction from asphaltene of the coal extract⁸⁾:

Five grams of isolated asphaltene (BS) was dissolved in 120 ml of toluene through which dry HCl gas was bubbled to precipitate HCl adduct. The adduct was washed with 25 ml of toluene four times (yield 2.8 g, N% 3.0).

2.5 Preparation of γ -picoline (and quinoline)-ZnCl₂ complex:

Methanol solution (40 ml) containing 20 g (0.2 mol) of γ -picoline was added, while stirring, to 100 ml methanol containing 13.6 g of ZnCl₂ (0.1 mol), to form 26 g of crude complex which on recrystallization from methanol gave a white crys-

talline product (mp 177–179°C): N%, 8.63 (8.69); M.W., 330 (323). By a similar procedure, quinoline-ZnCl₂ complex-(2:1) of mp 256–258°C and nitrogen content of 6.94 (7.10)% was obtained in a 92% yield.

2.6 Average structure by computer assisted molecular structure construction method (CAMSC):⁹⁾

The average structures of two coal extracts (0.5 hr and 3 hr) were estimated by the method proposed by Oka et al.

The nmr spectra were recorded on a JEOL JNM-PS-100 spectrometer in CDCl₃ solution using tetramethylsilane as the internal standard. The average molecular weight was determined in chloroform solution with a Hitachi Perkin Elmer 115 vapor pressure osmometer. Gc-ms was measured using a Hitachi RMU-6MG spectrometer at 20 eV connected to a Hitachi M 5201 apparatus using a 3 mm $\times$ 3 m column of 5% Silicon OV-1 on Uniport KS. Far-infrared spectra were taken using the apparatus described elsewhere.¹⁰⁾

3. Results and Discussion

3.1 Effects of extraction time on the resulting extract structure:

Depolymerization of Yūbari coal in tetralin was carried out at 400°C with an initial hydrogen pressure of 80 kg/cm² for 30 min and 3 hr, respectively. The analytical results of the two coal extracts are listed in **Table 1**. Duration of reaction does not change its molecular weight within the limits of experimental errors. However, a longer reaction time increases the H/C ratio from 0.83 to 0.86. These findings suggest that depolymerization of Yūbari coal in the presence of tetralin takes place within the first 30 min of the reaction, and the subsequent reaction is hydrogenation of the depolymerized coal materials. This is reflected in the relatively large decrease in the oxygen content of the coal extract obtained under a longer time of reaction. This oxygen is ascribed to the phenolic OH based on the acetylation method.¹¹⁾

Table 2 Distribution of Coal Extracts

Duration of Reaction	30 min	3 hr
Extracts		
PS	14%	22%
BS	55%	61%
BIS	31%	17%

Fig. 2 Average Structures of Yūbari Coal Extract

It is noted that nitrogen contents of the two extracts are constant, 2.2%, comparable to 2.1% of the original coal, while the oxygen contents of the extracts decrease markedly compared with the oxygen content of the original coal. It was very difficult to remove the nitrogen by this depolymerization reaction.

The results of Soxhlet extraction of the coal extracts are listed in Table 2 where it is found that prolonged reaction time brought about relatively large decreases in the amounts of PS and BS along with the decrease in the amount of BI. Hydrogenation of depolymerized coal material that brings about, for example, partial removal of oxygen and hydrogenation of extract structure by prolonged reaction time is considered to be assisting the conversion of BI to BS and to PS, and that of BS to PS. In an attempt to get a plausible image of structural change of the coal extracts by prolonged reaction time, the average structures of two coal extracts were estimated according to the method proposed by Oka et al.⁹⁾ Input data are represented as integral numbers based on the experimental data shown in parentheses. Data for CAMSC:coal extract(30 min), $H_a=8(8.6)$, $H_b=10(10.0)$, $H_{a1}=18(18.6)$, $H_{ar}=12(11.7)$, $C_{ar}=28(27.8)$, $C_{a1}=9(8.9)$, $OH=1$, M.W. 498; coal extract(3hr), $H_a=9(9.4)$, $H_b=11(10.5)$, $H_{a1}=20(19.9)$, $H_{ar}=12(12.2)$, $C_{ar}=28(28.0)$, $C_{a1}=9.0(9.4)$, $OH=1$, M.W. 506.

Although this method gives many plausible structures for both coal extracts, their typical structures are cited in Fig. 2. The inspection of the structures affords the following interesting features concerning what effect prolonged reaction time exerts on the structural change of the extracts:

Table 3 Hydrocracking of Coal Extracts^{a)}

Run No.	1	2	3	4	5
Catalyst	none	ZnCl ₂	ZnCl ₂ / CuCl	ZnCl ₂	ZnCl ₂ / CuCl
Catalyst/Feed (wt/wt)	—	0.1	0.1	1.0	1.0
Product					
Gas	13%	14	16	34	35
PSL	6	23	25	39	38
PSH	22	28	27	12	9
BS	55	28	25	1	1

a) 400°C, 3 hr, 100 kg/cm² (initial hydrogen pressure)

1) From the comparison of the average structures a) and b), prolonged reaction time does not change the degree of condensation of the extract structures; however, it increases alkyl substituents by losing their cycloaliphatic structure. 2) By comparing a') with b'), it can be concluded that prolonged reaction time causes the opening of the saturate part of methyl indane of structure a') to give an isopropyl group. Accordingly, hydrogenation, which takes place after coal depolymerization, could be grasped conceptually, not as hydrogenation of aromatic skeleton but as hydrogenation of the cycloaliphatic part leading to the carbon-carbon bond cleavage.

3.2 Hydrocracking of the coal extract over molten salts:

Table 3 gives the hydrocracking results of coal extracts obtained by short-residence-time extraction where pure ZnCl₂ and ZnCl₂-CuCl (3:2 mol ratio) were used as catalysts. Without catalyst, BI is 4 wt%, and the BS fraction remaining in the amount similar to that of the original coal extract. From this, most of the BI converts to gaseous products, PS, and BS under the reaction conditions. The characteristics of the molten salt catalyst for hydrocracking of the coal extracts are summed up as follows: 1) The use of massive amounts of pure ZnCl₂ and ZnCl₂-CuCl produced large quantities of gaseous products and PSL along with a considerable amount of undesired product, coke. 2) The presence of 10 wt% of pure ZnCl₂ and ZnCl₂-CuCl melt increased the yield of PS fraction together with gaseous products by increasing the yields of BS and BI fractions. 3) The results of ZnCl₂-CuCl are comparable to those of pure ZnCl₂ (yields of PS and BS) in spite of the superiority of the former catalyst to the latter for hydrocracking of phenanthrene. These facts were rationalized by referring to the presence in the coal extract of the phenolic group of polyaromatic compounds that increased greatly the reactivity toward hydrocracking over the molten salt catalyst and leveled

Table 4 Analysis of both PSH and BS

Run No.	1		2		3		4	5
Properties	PSH	BS	PSH	BS	PSH	BS	PSH	PSH
C%	88.3	89.6	90.0	89.7	89.7	90.5	91.4	90.8
H%	8.0	6.3	8.1	6.5	8.6	6.6	8.3	8.8
N%	1.4	2.2	0.5	1.2	0.6	1.1	0.0	0.0
O%	2.3	1.9	1.4	2.7	1.1	1.8	0.3	0.4
H/C	1.08	0.83	1.08	0.86	1.14	0.87	1.09	1.16
f_a	0.61	0.75	0.59	0.71	0.55	0.71	0.61	0.70
H_{aru}/C_{ar}	0.78	0.64	0.71	0.60	0.77	0.60	0.71	0.60
M. W.	265	466	264	412	262	420	273	268

a) Analysis of BS could not be conducted because of scarcity of amount.

Table 5 Chromatographic Separation of PSH and BS Fractions from Run 1, 2 and 3

Fractions Catalyst	PSH			BS		
	none	ZnCl ₂	ZnCl ₂ CuCl	none	ZnCl ₂	ZnCl ₂ CuCl
Saturates	8	7	10	1	1	2
Aromatics	40	63	66	34	47	50
Aromatics + Ether	2	1	1	3	13	19
Nitrogen Compounds	24	12	12	36	19	15
Hydroxyl Compounds	7	12	4	19	14	12

off the hydrocracking ability of the two melts. Without catalysts, BS did not show any change in the nitrogen content compared with that of the original coal extract.

3.3 Properties of PSH and BS fractions:

Table 4 summarizes the results of micro-analysis of PSH and BS fractions along with Brown-Ladner's structural parameters.

In the case of 10 wt% of pure ZnCl₂ or ZnCl₂-CuCl, the nitrogen percentage of PSH and BS was about a half of the original N content while the large amounts of melts thoroughly removed the nitrogen atom in PSH and in BS. The H/C ratio of PSH and of BS increase more with ZnCl₂-CuCl melt than with pure ZnCl₂. This trend was reflected in the decreasing values of f_a and in the increasing values of H_{aru}/C_{ar} with ZnCl₂-CuCl melt. PSH and BS fractions were separated into five fractions by column chromatography.¹²⁾ **Table 5** shows these results. The inspection of this table led to the conclusion that ZnCl₂-CuCl melt (10 wt%) was superior to pure ZnCl₂ for decreasing the amounts of heteroatom-containing fractions.

3.4 Hydrocracking of quinoline and γ -picoline over molten salt catalyst:

Through our extensive studies on hydrogenation of coal and coal related materials over the ZnCl₂-containing melt catalysts, it was found that ZnCl₂-containing melt catalysts were highly effective for

removing the nitrogen. This superiority of the melt for hydrodenitrogenation suggests that the complex formation of ZnCl₂ with nitrogen-containing basic compounds leads to the selective elimination of the nitrogen atoms incorporated in the aromatic rings.

Table 6 shows the results of hydrocracking of a mixture of quinoline and the same weight of ZnCl₂, and of quinoline-ZnCl₂(2:1) complex.

The gc-ms analysis of liquids products could not detect any nitrogen-containing compounds. The two main products, cyclohexane and benzene derivatives, suggests that cracking proceeds via the formation of decahydroquinoline and tetrahydroquinoline. Hydrocracking of quinoline with an equivalent mol of ZnCl₂ at 400°C shows the two main products cited above, and their distribution is similar to that of hydrocracking of the quinoline-ZnCl₂ complex. A closer similarity was observed in the product distribution between run 6 and run 8, suggesting the above consideration concerning the removal of nitrogen atoms could be valid.

In order to confirm the complex formation of the nitrogen atoms in coal extracts with ZnCl₂, the basic fraction of nitrogen-containing concentrate was separated by the method of Bockrath et al.⁸⁾ Using the procedure similar to that for preparation of quinoline-ZnCl₂, this basic fraction was mixed with ZnCl₂ in methanol solution, and

Table 6 Hydrocracking of Quinoline and Quinoline-ZnCl₂ Complex

Starting Material	Quinoline Run 6	Quinoline-ZnCl ₂ Complex Run 7	Quinoline-ZnCl ₂ Complex Run 8
Catalyst Catalyst/Feed (mol/mol)	ZnCl ₂ 1.5	— 0.5	ZnCl ₂ 1.5
Gas	14.9 wt%	8.9	15.1
C ₅ -C ₇	4.2	1.1	2.8
$\left. \begin{array}{l} \text{---} \text{R (H, C}_1\text{)} \\ \text{---} \text{R (H, C}_1\text{-C}_4\text{)} \\ \text{---} \text{R (H, C}_1\text{-C}_3\text{)} \end{array} \right\}$	49.7	35.9	50.1
Others	28.0	23.7	27.3
	18.1	39.3	19.8

a) 400°C, 3 hr, 100 kg/cm² (initial hydrogen pressure)

Fig. 3 Far Infrared Spectra of Following Compounds

later the methanol was removed completely.

Figure 3 shows far-infrared spectra of the basic fraction alone(a), ZnCl₂-treated basic fraction(b), quinoline-ZnCl₂ complex (c), and γ -picoline-ZnCl₂ complex (d); the two complexes show strong absorptions which can be attributed to the stretching of the Zn-N bond in the region from 210 to 190 cm⁻¹. A comparison of the spectrum of the basic fraction alone and that treated with ZnCl₂ clearly shows the presence of a broad band ranging from 220 to 180 cm⁻¹ in the latter. This range of broadness can be considered as the envelop of many absorptions of such complexes because the fractions have many types of nitrogen-containing

groups due to the complex properties of the extracts.

4. Conclusion

- (1) In the preparation of coal extracts, prolonged reaction time slightly decreases the molecular weight. The ring opening of the alicyclic parts of extracts probably takes place.
- (2) The ZnCl₂-CuCl system is superior to ZnCl₂ in increasing the amounts of lower hydrocarbons (PSL), especially when it is used in 10 wt percent.
- (3) Higher H/C and H_{aru}/C_{ar} ratios and lower f_a of PSH and BS in the products of hydrocracking over ZnCl₂-CuCl melt compared to that over ZnCl₂ suggest a higher hydrocracking activity of ZnCl₂-CuCl than that of ZnCl₂.
- (4) The chromatographic separation of PSH and BS shows that ZnCl₂-CuCl melt is more effective than ZnCl₂ melt for eliminating the heteroatoms of coal extracts.
- (5) The hydrocracking behavior and far-infrared spectra of the quinoline-ZnCl₂ complex strongly suggest that reaction for elimination of the nitrogen atoms in coal extracts proceeds via the complex formation with ZnCl₂.

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要 旨

タ張炭の解重合反応と抽出物の水素化分解におよぼす ZnCl_2 溶融塩の触媒作用

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タ張炭の可溶化反応をテトラリン存在下 400°C, 水素初期圧 80 kg/cm², 反応時間 30 分および 3 時間で行った。抽出物の調製方法は Fig. 1 に示し, Table 1 にはおのおの抽出物の元素分析値, 構造パラメーター, H/C 比, 平均分子量値を掲げた。反応時間を 30 分から 3 時間に延長した場合の効果をみると平均分子量値にほとんど変化がなく, 酸素含量の低下と H/C 比の増大がみられた。このことから水素化分解と脱酸素反応が進行していると考えられる。溶剤分別の結果 (Table 2) から時間が経つと BS や PS が増加することがわかる。電算機を利用した各抽出物の平均構造 (Fig. 2) をみると, 構造 a (3 時間) と b (30 分) の比較から脂環部分の開裂によるアルキル基の増加が推測される。長時間反応の石炭可溶化への影響を, a' と b' の比較から脂環部分が水素化分解をうけ, イソプロピル基等で置き変わるというイメージでとらえられる様に思われる。反応時間 30 分の抽出物を対象に ZnCl_2 および $\text{ZnCl}_2\text{-CuCl}$ 溶融塩を触媒に水素化分解を行った結果を Table 3 に示した。結果は以下の様にまとめられる。1) 多量の塩の使用はガス状生成物と PSL を増加させる。2) 10 wt% の塩の使

用は PS 分を増加させる。3) $\text{ZnCl}_2\text{-CuCl}$ は ZnCl_2 に比べフェナンスレンの水素化分解に著しく高い活性を示したにもかかわらず, 石炭抽出物では両者に活性の差が余りみられない。抽出物に存在するフェノール性 OH が芳香族環の水素化分解に対する活性を高めたためと考えられる。

PSH と BS の分析結果 (Table 4) から 10 wt% の塩は窒素%を著しく低下させ, 等量の塩を使用すると窒素は完全に除去される。PSH と BS をカラムクロマトグラフで分別した結果 (Table 5) から $\text{ZnCl}_2\text{-CuCl}$ 塩は ZnCl_2 塩に比べ, ヘテロ原子の除去に極めて優れていることがわかる。Nを含むモデル化合物としてキノリンおよび γ -ピコリンと ZnCl_2 のコンプレックス (2:1) を合成, 前者の水素化分解を行った (Table 6)。液体生成物には GC-MS から窒素を含む化合物が認められず, コンプレックスの水素化分解による生成物分布は等量の ZnCl_2 存在下での結果とよく類似しており, 特に Run 8 の生成物分布は Run 6 とほぼ一致することから窒素化合物は ZnCl_2 とコンプレックスをつくり分解してゆくと考えられる。抽出物の塩基成分を ZnCl_2 で処理したものの遠赤外スペクトル (Fig. 3) から Zn-N 伸縮が強度は弱いが 180-220 cm⁻¹ にみられ, 上記の推論を裏づける結果を与えることができた。

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