Effectiveness of ZnCl_2 - KCl - NaCl - MoCl_5 Melt for Hydrocracking of Athabasca Oil Sand Bitumen and Significance of Resin Fraction on Coke Formation

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Athabasca oil sand bitumen was hydrocracked over ZnCl_2 - KCl - NaCl melt and ZnCl_2 - KCl - NaCl - MoCl_5 melt at temperatures from 350°C to 400°C for 3 hours with an initial hydrogen pressure of 100 kg/cm². In respect of distribution of products such as gas, pentane soluble (PS) and benzene soluble (BS), ternary melt catalyzed run at 375°C is roughly equal to the run without catalyst at 400°C, while the runs at 375°C and 400°C with the ternary melt are similar to the ones at 350°C and 375°C with the quaternary melt, respectively (assuming the sum of gas and PS as light hydrocarbon). Elementary analyses, a simulated distillation and chromatographic separation of the resulting PS, clarified the characteristics of the melt catalyst: 1, the degree of hydrodesulfurization increases from without catalyst to the quaternary melt via the ternary melt; 2, a simulated distillation confirms that the ternary melt at 375°C is roughly equivalent to the quaternary melt at 350°C; 3, the quaternary melt is excellent in assisting hydrogenation of polyaromatics and removal of heteroatoms. The coke formation, accompanied with hydrocracking of bitumen, might be attributed partly to resin fraction, besides asphaltene fraction, based on hydrocracking of maltene and resin, and structural study of the resulting PS fraction from resin.

1. Introduction

The Athabasca bitumen is a heavy, sulfurous oil with high content of asphaltene which is believed to be strongly responsible for coke formation accompanied with pyrolytic processes such as delayed- and fluid-coking. Speight et al.¹⁾ described that thermal cracking of the deasphalted heavy oil also produced much coke as well as that of asphaltene itself while Nandy et al.²⁾ stated that coke formed during thermal hydrocracking of bitumen could be differentiated as one having deasphalted heavy oil as its origin and one having asphaltene as its origin, respectively, based on microscopic study.

In a previous paper,³⁾ we have reported that ZnCl_2 - KCl - NaCl - MoCl_5 melt (3 : 1 : 1 : 1 mol ratio) shows excellent catalytic effect in suppressing coke formation on hydrocracking of Athabasca oil sand asphaltene.

The purpose of this paper is to examine the effectiveness of ZnCl_2 - KCl - NaCl - MoCl_5 melt on

hydrocracking of oil sand bitumen. It will be shown that the maltene fraction also produces coke, even in the presence of above melt catalyst, and that polar fraction of maltene is supposed to play a significant role in coke formation.

2. Experimental

2.1 Reagents

Zinc chloride and molybdenum pentachloride (guaranteed reagent grade) were obtained from Nakarai Chemicals, Ltd. and Mitsuwa Pure Chemicals, Co. Ltd., respectively. These salts were dried at 120°C for 3 hours under vacuum (20 mmHg) prior to use. Floridil (100 mesh, from Wako Pure Chemicals, Co. Ltd.) used for separation of resin fraction was heated for 3 hours at 150°C before use. Organic solvents employed here were purified by conventional procedures.

2.2 Preparation of Bitumen, Maltene and Resin

Athabasca oil sand (from Suncor Ltd., Fort McMurray, Alberta, Canada) 500g, was extracted

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with benzene and the bitumen (77g) was freed from benzene by evaporation. The bitumen was separated into maltene (67g) and asphaltene (10g) by the standard method⁴⁾, *n*-pentane precipitation. Twenty five grams of maltene thus prepared were separated on activated Floridil (250 g) by elution chromatography using a column 70 cm × 40 mm i.d.: the oil component were first removed by elution with 3 l of *n*-pentane. The resin component was defined as the material that remained on the column after the pentane elution.⁵⁾ These were eluted by methanol(2.5 l) and benzene(1.5 l). The solvent was removed from each fraction by distillation at reduced pressure. Analyses results of bitumen : C 82.0, H 10.5, N 0.5, S 4.8, O 2.2% ; Analyses results of maltene : C 84.4, H 11.1, N trace, S 3.7, O 0.8% ; Analyses results of resin ; C 80.3, H 9.5, N 0.7, S 6.1, O 3.4%.

2.3 Hydrocracking of Bitumen, Maltene and Resin

Bitumen (or maltene or resin) was added, while being stirred, to methanol solution containing the determined amounts of melt constituents, methanol being completely removed from the mixture. These mixtures were placed in a 200 ml autoclave (Hastelloy F) which was flushed three times with hydrogen gas and pressurized to 100 kg/cm² at room temperature. The autoclave mounted in a furnace was heated at a rate of 3°C/min to reach the desired temperature (about 1.5 h). The autoclave was kept at that temperature for 3 hours. After the end of reaction, a portion of the gas phase (at room temperature) was vented into a 18 l gas storage, aliquots of which were submitted to gas chromatographic analysis. Then the contents of autoclave were Soxhlet-extracted with *n*-pentane for 20 h, followed with benzene for 20 h. For sake of convenience, a pentane-soluble portion, a benzene-soluble and pentane-insoluble portion, and a benzene-insoluble portion will be termed PS, BS (asphaltene) and BI(coke), respectively. Melt constituents remained on coke was eliminated by treatment with 6N HNO₃.

2.4 A Simulated Distillation of the Resulting PS from Bitumen

A simulated distillation of PS fraction, in accordance with the procedure of ASTM D 2887-73, was undertaken, using a Shimadzu GC-4BPTF gas chromatograph equipped with thermal conductivity detector [column : Silicon OV-1 (4.5 m), 30—270°C programmed at 2.5°C/min]. From the calibration curve obtained using *n*-paraffine peaks

(C₈–C₃₁), there were assigned boiling temperatures at appropriate intervals at which area measurements were made.

2.5 Chromatographic Separation of the Resulting PS from Bitumen

PS fractions were submitted to liquid chromatographic separation according to the methods of Sawatzky et al.⁶⁾ which separates them into saturates, monoaromatics, diaromatics, polyaromatics, and polar compounds. The amount of each fraction is presented in terms of wt% (Table 4) based on bitumen charged.

2.6 Average Structural Parameters of the Resulting PS

From ¹H n.m.r. spectra, elemental analyses and the average molecular weight, structural parameters were computed according to the procedure of Brown and Ladner.⁷⁾ 100 MHz ¹H n.m.r. spectra were recorded on a JNM-PS-100 NMR spectrometer in CDCl₃ with TMS as an internal standard. The average molecular weight was determined by using a Mecrolab vapour-phase osmometry in CHCl₃ solution.

3. Results and Discussion

3.1 Hydrocracking of Athabasca Oil Sand Bitumen

In a previous paper,³⁾ we mentioned having applied ZnCl₂–KCl–NaCl (3 : 1 : 1 mol ratio) and ZnCl₂–KCl–NaCl–MoCl₅ melts as hydrocracking catalysts for asphaltene at 400°C. Here bitumen was hydrocracked at 350, 375 and 400°C in the absence of catalysts.

Figure 1 shows the dependence of gas, PS, BS, and coke yields on reaction temperature. As

Fig. 1 Dependence of Products Yield on Reaction Temperatures

temperature increases, the yield of gas increases and that of BS decreases while PS yields being almost constant. At 400°C, coke appeared, probably as a result of severe reaction conditions.

Hydrocracking of bitumen in the presence of $\text{ZnCl}_2\text{-KCl-NaCl}$ melt, both at 375 and 400°C, suggests that PS yield reaches 85.1% at 375°C along with 4.1% gas yield, while at 400°C, PS yield decreases and gaseous product increases (**Table 1**). Since 14.8% of gas yield was attained at 400°C, this temperature seems not to be appropriate with this melt catalyst for attaining high PS yield.

Two reaction temperatures (350 and 375°C) were examined for hydrocracking of bitumen in the presence of $\text{ZnCl}_2\text{-KCl-NaCl-MoCl}_5$ melt.

A comparison, among three temperatures without catalyst and two temperatures with the ternary melt in **Table 1**, reveals that in product distribution, the result of experiment at 375°C using $\text{ZnCl}_2\text{-KCl-NaCl}$ catalyst is closer to that of experiment using no catalyst at 400°C.

On the other hand, the product distribution of $\text{ZnCl}_2\text{-KCl-NaCl-MoCl}_5$ catalyzed experiment (375°C) appears to be relatively different from that of $\text{ZnCl}_2\text{-KCl-NaCl}$ catalyzed experiment (400°C), especially in respect of gas and PS yields. However, if taking into account that PS partly converts to gaseous product because of thermal and catalytic degradation and that the sum of gas and PS yields represents light hydrocarbon fraction produced by catalytic hydrocracking, product distribution cat-

alyzed by $\text{ZnCl}_2\text{-KCl-NaCl}$ at 400°C and 375°C somewhat resembles that catalyzed by $\text{ZnCl}_2\text{-KCl-NaCl-MoCl}_5$ at 375°C and 350°C, respectively.

Table 2 cites the simulated distillation of PS derived from hydrocracking of bitumen. It should be noted that distribution of five distillates from $\text{ZnCl}_2\text{-KCl-NaCl}$ catalyzed experiments at 400°C is very close to those from $\text{ZnCl}_2\text{-KCl-NaCl-MoCl}_5$ catalyzed experiment at 375°C. Those between $\text{ZnCl}_2\text{-KCl-NaCl}$ catalyzed experiment at 375°C and $\text{ZnCl}_2\text{-KCl-NaCl-MoCl}_5$ catalyzed experiment at 350°C is not as similar as observed above: distillates of the former have slightly higher boiling fraction than those of the latter. However these findings suggest that the $\text{ZnCl}_2\text{-KCl-NaCl-MoCl}_5$ system is excellent in promoting hydrocracking of heavy carbonaceous materials compared with $\text{ZnCl}_2\text{-KCl-NaCl}$ system.

3.2 Properties of PS Fractions

In order to evaluate melt catalysis, we have to consider the quality of PS fraction as well as its amounts. Especially, since Athabasca oil sand bitumen contain a great amount of sulfur, it is important to examine the amounts of sulfur in PS fractions.

Table 3 lists the analysis of PS fraction. Without using catalyst, amounts of sulfur in PS range between 3.1—3.8% while use of catalyst reduces this amount to 2.1% with $\text{ZnCl}_2\text{-KCl-NaCl}$ (400°C) and 1.7% with $\text{ZnCl}_2\text{-KCl-NaCl-MoCl}_5$ (375°C). The quaternary melt is found to be more effective in removing sulfur in bitumen. At the same time, atomic

Table 1 Hydrocracking of Oil Sand Bitumen

Catalyst	Temperature	Products (wt%)			
		Gas	PS	BS	BI
none	350°C	0.8	84.2	15.0	trace
	375°C	3.2	83.8	13.0	trace
	400°C	4.7	84.3	7.4	3.6
$\text{ZnCl}_2\text{-KCl-NaCl}$	375°C	4.1	85.1	8.0	2.8
	400°C	14.8	77.9	2.8	4.5
$\text{ZnCl}_2\text{-KCl-NaCl-MoCl}_5$	350°C	9.7	80.2	6.9	3.2
	375°C	9.6	83.4	3.4	3.6

Table 2 Simulated Distillation of PS Fraction

Catalyst	Temperature (°C)	Boiling Range				
		—100°C	100—200°C	200—300°C	300—400°C	400°C—
$\text{ZnCl}_2\text{-KCl-NaCl}$	375	trace	2.3%	21.2%	44.4%	32.1%
	400	trace	12.0	35.3	36.6	16.1
$\text{ZnCl}_2\text{-KCl-NaCl-MoCl}_5$	350	0.2%	8.0	28.2	37.9	25.7
	375	0.3	12.3	36.1	36.5	14.8

Table 3 Elemental Analysis of PS Fraction

Catalyst	Temperature (°C)	C %	H %	N %	S %	O %	H/C
none	350	84.2	11.1	0.3	3.1	1.3	1.57
	375	83.3	10.9	0.0	3.8	2.0	1.56
	400	84.7	11.1	0.4	3.3	0.5	1.56
ZnCl ₂ -KCl-NaCl	375	85.2	11.3	0.0	2.9	0.6	1.58
	400	86.0	11.3	0.0	2.1	0.6	1.57
ZnCl ₂ -KCl-NaCl-MoCl ₅	350	85.8	11.7	0.0	2.0	0.5	1.62
	375	86.0	11.6	0.0	1.7	0.7	1.61

Table 4 Chromatographic Separation of PS Obtained at 375°C

Catalyst	Saturates	Monoaromatics	Diaromatics	Polyaromatics	Polar Compound
none	22.5 ^{a)} (26.8) ^{b)}	12.8 (15.3)	8.5 (10.1)	16.0 (19.2)	24.0 (28.6)
ZnCl ₂ -KCl-NaCl	34.5 (40.5)	13.5 (15.9)	14.2 (16.7)	12.9 (15.2)	10.0 (11.7)
ZnCl ₂ -KCl-NaCl-MoCl ₅	40.5 (48.6)	13.4 (16.1)	15.7 (18.8)	7.6 (9.1)	6.2 (7.4)

^{a)} Wt% on the basis of bitumen

^{b)} Distribution % in PS

ratio of H/C in PS increases slightly from none catalyzed run to the ternary melt catalyzed run and this increment of H/C from the ternary melt catalyzed run to the quaternary melt catalyzed run are apparent. This trend is also in an agreement with the following results of chromatographic separation of PS (**Table 4**): high atomic ratio of H/C reflects high yields of saturates fraction obtained with ZnCl₂-KCl-NaCl-MoCl₅ melt. The comparison of three experiments, without catalyst, with ZnCl₂-KCl-NaCl, and ZnCl₂-KCl-NaCl-MoCl₅ melts indicate that saturates and diaromatics increase in the following order, without catalyst, ZnCl₂-KCl-NaCl melt, ZnCl₂-KCl-NaCl-MoCl₅ melt, while polyaromatics and polar compounds decrease in this order. These observations implies that ZnCl₂-KCl-NaCl-MoCl₅ system is excellent in both hydrogenating condensed aromatic rings and removing heteroatoms.

3.3 Hydrocracking of Maltene and Resin

We have carried out hydrocracking of maltene fraction at the same reaction conditions as applied for hydrocracking of bitumen [375°C, 3 h, 100 kg/cm² (H₂)]. **Table 5** lists the hydrocracking of oil sand maltene. As far as coke amount is concerned, wt% of coke yield from hydrocracking of bitumen exceeds the corresponding amounts of coke derived from the hydrocracking of maltene at same reaction conditions, the increment of coke yield with bitumen being attributed to the asphaltene fraction. Relatively high yield of coke observed in the hydrocracking of maltene, a deasphalted fraction, suggests that resin fraction plays a significant role in coke formation as well as asphaltene in the

hydrocracking of bitumen, because resin contained in maltene fraction is believed to go through a structural transition from the complex polar asphaltenes to the less polar hydrocarbon matrix(oil) and to serve to disperse effectively the asphaltene in oil fraction.⁸⁾ Resin fraction, therefore, is supposed to be the most probable precursor of the coke produced in hydrocracking of maltene.

Table 6 shows the result of hydrocracking of resin which clarifies above estimation to be true. Participation of oxygen- and sulfur-related functional groups of resin²⁾ in coke formation, therefore, is highly probable.

In order to study the structural properties of PS fraction produced from resin, its average structural parameters were referred to. **Table 7** lists the aromaticity f_a , the ratio H_{aru}/C_{ar} of peripheral aromatic carbons to total aromatic carbons, and

Table 5 Hydrocracking of Oil Sand Maltene (375°C)

Catalyst	Products (wt%)			
	Gas	PS	BS	BI
none	2.3	95.7	2.0	trace
ZnCl ₂ -KCl-NaCl	3.8	91.1	3.8	1.3
ZnCl ₂ -KCl-NaCl-MoCl ₅	15.1	81.7	0.6	2.6

Table 6 Hydrocracking of Oil Sand Resin (375°C)

Catalyst	Products (wt%)			
	Gas	PS	BS	BI
none	5.5	88.4	5.8	0.3
ZnCl ₂ -KCl-NaCl	10.4	76.0	8.5	5.1
ZnCl ₂ -KCl-NaCl-MoCl ₅	11.8	81.3	2.3	4.6

Table 7 Structural Parameters of PS Fraction

Material	Catalyst	f_a	σ	H_{aru}/C_{ar}
Bitumen	none	0.34	0.70	0.70
	ZnCl ₂ -KCl-NaCl	0.34	0.57	0.62
	ZnCl ₂ -KCl-NaCl-MoCl ₅	0.33	0.59	0.73
Resin	none	0.40	0.56	0.85
	ZnCl ₂ -KCl-NaCl	0.41	0.51	0.88
	ZnCl ₂ -KCl-NaCl-MoCl ₅	0.42	0.49	0.84

the degree of substitution σ , i.e. the fraction of peripheral aromatic carbons that are substituted, by customary procedure of Brown-Ladner. These values are computed by taking the corrected term 2 (O+S+N) into consideration.⁹⁾

With PS from bitumen, H_{aru}/C_{ar} ranges from 0.62 to 0.73, while this value is from 0.84 to 0.88 with resin-derived PS, H_{aru}/C_{ar} , 0.9, indicates that the products contain a mixture of one ($H_{aru}/C_{ar}=1$) aromatic ring and two ($H_{aru}/C_{ar}=0.8$) condensed aromatic ring units while H_{aru}/C_{ar} , 0.71 being three condensed aromatic ring ($H_{aru}/C_{ar}=0.714$) in the case of bitumen-derived PS. Resin, therefore, has relatively small ring unit compared with that of bitumen. Further, the great degree of coke formation in the case of hydrocracking of resin can, perhaps, be attributed to both the effect of polar groups contained, which can promote cross-linking by heteroatom containing bond formation,

and to such a possible conversion of cycloalkane ring to polycondensed aromatic rings, as we have already suggested.¹⁰⁾

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要 旨

アサバスカオイルサンドビチューメンの水素化分解におよぼす $\text{ZnCl}_2\text{-KCl-NaCl-MoCl}_5$ 塩触媒の効果と炭化物生成に対するレジンの寄与野 村 正 勝^{†1)}, 岡 敏 夫^{†2)}^{†1)} 大阪大学工学部応用化学科, 565 吹田市山田丘 2-1^{†2)} ダイセル化学工業(株), 661 尼崎市神崎町 12-1

200 ml のオートクレーブを用いオイルサンドビチューメンを水素初期圧 100 kg/cm² で 350, 375 および 400°C で 3 時間反応させた。Fig. 1 に無触媒でのペンタン可溶部 (PS), ペンタン不溶-ベンゼン可溶部 (BS) およびベンゼン不溶部 (BI) の生成率を各反応温度に対してプロットした。BI は 400°C で生成する。Table 1 には無触媒, $\text{ZnCl}_2\text{-KCl-NaCl}$ (3:1:1 モル比) および $\text{ZnCl}_2\text{-KCl-NaCl-MoCl}_5$ (3:1:1:1 モル比) 存在下での水素化分解結果を示した。

3 元系塩では反応温度を 375 から 400°C に変えるとガスは 4.1 から 14.8% に増加する。3 元系塩 375°C での生成物分布は無触媒 400°C でのそれと類似し, ガスと PS を軽質物と考えると 3 元系塩 375, 400°C の生成物分布は 4 元系塩 350, 375°C のそれとよく一致する。

塩の触媒作用を評価するためにビチューメンの水素化分解によりえられた PS 留分の模擬蒸留を行い 5 つの沸点範囲の留分に分けたが (Table 2), 3 元系塩 400°C の沸点範囲の分布が 4 元系塩 375°C のそれによく一致することがわかった。Table 3 に PS 留分の元素分析を示し Table 4 に PS 留分の液体クロマト分析 (シリカ-アルミナ) による飽和脂肪族分, 単環芳香族分, 二環芳香族分, 多環芳香族分, 極性化合物への分離結果

を示した (Table 4)。Table 3 から PS の脱硫黄は無触媒 < 3 元系塩 < 4 元系塩と増加した。一方 Table 4 から無触媒, 3 元系塩, 4 元系塩になるにつれて飽和脂肪族と二環芳香族の増加が, また極性化合物と多環芳香族が減少した。このことから 4 元系塩は多環芳香族の水素化とヘテロ原子の除去にすぐれていることがわかった。

マルテンの水素化分解結果を Table 5 に示した。3 元系塩, 4 元系塩での BI の生成量は対応する ビチューメンからの量 (Table 1) に比べ小さいが, レジンの水素化分解結果 (Table 6) と併せて考えると ビチューメンの水素化分解で生成するコークはアスファルテンの他にレジン分に由来することが結論できる。

ビチューメンおよびレジンの水素化分解からの PS の平均構造を Table 7 に示した。この結果無触媒, 3 元系塩, 4 元系塩共にビチューメンからの PS は 3 環芳香族骨格を持つと考えられるのに対し, レジンからの PS は単環芳香族と 2 環芳香族骨格の存在が考えられ, このことからレジンからの BI は極性グループによる架橋ないしシクロアルカン部の脱水素による縮合芳香環の生成がその原因と推察される。

Keywords

Coke formation, Hydrocracking, Molten salt catalyst, Oil sand bitumen, Resin