Catalytic Effects of $MoCl_3$- and $NiCl_2$-Containing Molten Salts for Hydroliquefaction of Morwell Brown and Taiheiyo Subbituminous Coals

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The catalytic effects of $MoCl_3$–LiCl–KCl and $NiCl_2$–LiCl–KCl molten salts were studied for the hydroliquefaction of Morwell brown and Taiheiyo subbituminous coals at 400 °C for 1 h in a batch reactor with an initial hydrogen pressure of 9.8 MPa. The conversion to pyridine-soluble materials and the yield of hexane-soluble materials (HS) with the $MoCl_3$ catalyst were 82 and 42% for Morwell coal, and 84 and 61% for Taiheiyo coal, respectively. The conversion and HS yield with the $NiCl_2$ catalyst were 87 and 43% for Morwell coal, and 82 and 56% for Taiheiyo coal, respectively. The HS yield of the catalytic runs was about 2.6—3.2 times higher than that of noncatalytic runs. This finding established the effectiveness of the two new catalysts for the hydroliquefaction of brown and subbituminous coals. Detailed analyses of the reaction products have revealed that these catalysts promoted a depolymerization of the coals and strongly catalyzed the hydrocracking of polynuclear aromatic structures of heavy products into hydroaromatic and aromatic structures with smaller ring sizes. Most of these smaller hydroaromatic and aromatic structures did not undergo much further ring-opening reactions. This accounts for the high HS selectivity of the catalysts.

One of the most promising approaches to the development of coal liquefaction processes is the development of new and novel catalytic systems.[1] We have previously found[2] that $MoCl_3$– and $NiCl_2$–LiCl–KCl molten salts acted as excellent hydrocracking catalysts for the hydroliquefaction of an Australian subbituminous coal (Wandoan). Since different ranks of coal generally show different reactivities toward hydroliquefaction, it is necessary to examine the effectiveness of these new catalysts for the hydroliquefaction of other coals different from Wandoan coal.

Two coals, Morwell brown coal (Australia) and Taiheiyo subbituminous coal (Japan), which have lower carbon contents and higher oxygen contents compared with Wandoan coal, were used in the present work. This paper reports on the hydroliquefaction of Morwell and Taiheiyo coals over $MoCl_3$–LiCl–KCl and $NiCl_2$–LiCl–KCl molten salt catalysts; their catalysis is characterized by a detailed analytical study of the reaction products.

Experimental

Reagents and Materials. Morwell brown and Taiheiyo subbituminous coals were used in the present work. The coals were pulverized to <74 μm and then stored under an N_2 atmosphere. Proximate and ultimate analyses of the coals are listed in Table 1. For each experiment the required quantity of coal was dried at 105 °C in vacuo for 1.5 h before use. The examined catalysts were $MoCl_3$–LiCl–KCl (molar composition, 12:51:37; eutectic temperature, 387 °C) and $NiCl_2$–LiCl–KCl (14:54:36; 360 °C) ternary molten salts. $MoCl_3$ was synthesized according to a procedure proposed by Mallock,[3] except that resulting $MoCl_3$ was further purified by washing with distilled methanol. The X-ray diffraction pattern of thus-purified $MoCl_3$ is very consistent with that of literature.[4] The $MoCl_3$ and guaranteed reagent-grade $NiCl_2$, LiCl, and KCl were used as salt constituents of the catalysts. For each experiment the required quantity of catalyst was dried at 140 °C in vacuo for 6 h before use. Guaranteed reagent-grade hexane, benzene and pyridine were used as received.

Hydroliquefaction Procedures. Hydroliquefaction reactions were carried out in a 200 ml batch autoclave (SUS 316) that was shaken horizontally. In a typical run, coal was impregnated with the same weight of catalyst by immersing the coal into a methanol solution or a suspension in methanol followed by drying at 105 °C in vacuo for more than 6 h. Thus-treated coal was placed into an autoclave. Hydroliquefaction was carried out at 400 °C for 1 h with an initial hydrogen pressure (cold) of 9.8 MPa (100 kg cm^{-2}). After the reaction, products were separated into gases consisting of C_1–C_4 hydrocarbons and CO_x ($CO+CO_2$), hexane-soluble fraction (HS), hexane-insoluble and benzene-soluble fraction (BS), benzene-insoluble and pyridine-soluble fraction (PyS) and pyridine-insoluble fraction (PyI). The HS, BS, and PyS fractions are denoted as oil, asphaltene and preasphaltene, respectively. Details of the procedures have been described elsewhere.[2] The yield of products,

Table 1. Representative Analyses of Coals

Coal	Morwell	Taiheiyo
Proximate (wt%)		
Volatile matter	41.4	45.5
Fixed carbon	37.4	33.9
Ash	1.6	14.5
Moisture	19.6	6.1
Ultimate (wt%, daf)		
Carbon	67.4	76.1
Hydrogen	5.0	6.7
Nitrogen	0.5	1.5
Sulfur	0.3	0.2
Oxygen (by difference)	26.8	15.5

conversion and amount of hydrogen consumed were calculated on a d.a.f. coal basis.

Analytical Method of Products. The HS and BS fractions obtained from the hydroliquefaction of the two coals were subjected to elemental and ^{1}H NMR analyses. The ^{1}H NMR spectra were measured in a $CDCl_3$ solution with tetramethylsilane as an internal standard using a JNM-PS-100 spectrometer operating at 100 MHz. Deuterium oxide was added to some of the solutions of HS and BS fractions in order to identify the phenolic OH resonance; contribution from overlapping signals was then subtracted. The integrated intensity from all the hydrogen was divided into several parts, which could be assigned to the hydrogen of different chemical environments. A distribution of hydrogen types was calculated as the numbers of hydrogen atoms per 100 carbon atoms from the ^{1}H NMR data and elemental analysis. The average structural parameters of the HS and BS fractions were calculated based on Brown-Ladner equations[5] from the data of ^{1}H NMR and elemental analyses.

Results

Hydroliquefaction of Coals. Table 2 gives conversion and H_2 consumption values and Fig. 1 shows the product distribution of the hydroliquefaction of Morwell brown and Taiheiyo subbituminous coals. Without a catalyst, the hydroliquefaction of Morwell and Taiheiyo coals gave relatively low conversions (66.0—67.8%) with low H_2 consumptions (0.7—0.9%). The use of both $NiCl_2$-LiCl-KCl and $MoCl_3$-LiCl-KCl catalysts considerably increased the coal conversion and H_2 consumption, indicating the great effectiveness of these catalysts for converting brown and subbituminous coals.

The increases in the conversion and H_2 consumption with the $MoCl_3$ and $NiCl_2$ catalysts (Table 2) were accompanied by pronounced changes in the product distribution (Fig. 1); the important features of the catalytic runs compared with noncatalytic runs are considerably decreased PyI and PyS yields and greatly increased HS yield. The net production of HS was, as would be expected,[6-7] lower with Morwell brown coal than with Taiheiyo subbituminous coal.

Table 2. Hydroliquefaction of Morwell and Taiheiyo Coals

Run No.	Coal	Catalyst	Conversion[a] (wt%, daf)	H_2 consumed (wt%, daf)
1	Morwell	None	66.0	0.7
2	Morwell	$NiCl_2$-LiCl-KCl	86.8	3.6
3	Morwell	$MoCl_3$-LiCl-KCl	82.4	5.5
4	Taiheiyo	None	67.8	0.9
5	Taiheiyo	$NiCl_2$-LiCl-KCl	82.3	4.0
6	Taiheiyo	$MoCl_3$-LiCl-KCl	84.0	4.7

a) Conversion = (1-PyI/coal) × 100%.

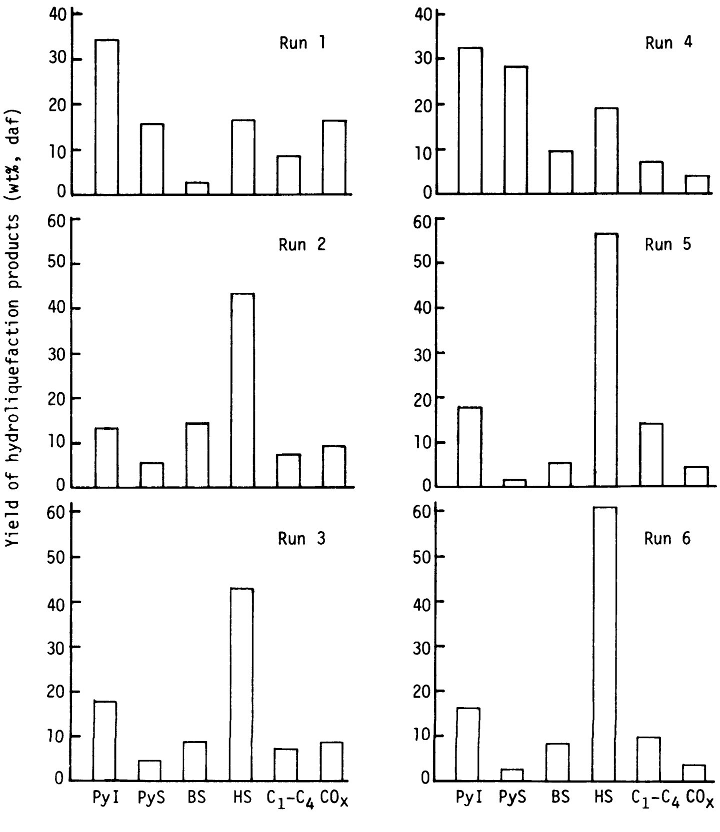

Fig. 1. Product distribution of hydroliquefaction of Morwell and Taiheiyo coals. See Table 2 for run number.

However, it should be noted that relative to noncatalytic runs of the two coals, both the $MoCl_3$ and $NiCl_2$ catalysts selectively enhanced the production of the HS yield without a significant change in the C_1–C_4 gas yield.

Elemental Analysis. Table 3 shows the results of an elemental analysis of the HS and BS fractions. The HS of the catalytic runs had a little higher carbon content, a lower hydrogen content and a lower H/C atomic ratio than that of noncatalytic runs. The content of heteroatoms (N+O+S) of the former was lower or similar to that of the latter. In runs involving Morwell coal, nitrogen was completely removed from the HS by the use of both catalysts. On the other hand, more heteroatoms were retained in the BS of catalytic runs, as compared with its corresponding HS.

^{1}H NMR Spectroscopy. Table 4 gives assignments of ^{1}H NMR spectra bands of HS and BS. The assignments are based on both the chemical shifts of the model compounds[8)] containing structures that are believed to be present in coal-derived products and some other assignments found in the literature.[9—12)]

Table 3. Elemental Analysis of HS and BS from Morwell and Taiheiyo Coals

Run No.	Product	C	H	N	O+S[a)]	H/C
		wt%				
1	HS	85.3	9.0	0.4	5.3	1.25
	BS	85.0	6.7	0.7	7.6	0.94
2	HS	87.9	8.9	—	3.2	1.20
	BS	86.7	6.6	1.0	5.7	0.91
3	HS	87.4	8.7	—	3.9	1.19
	BS	83.4	6.4	0.9	9.3	0.92
4	HS	85.2	10.2	0.4	4.2	1.43
	BS	87.6	6.9	1.3	4.2	0.94
5	HS	86.3	8.9	0.3	4.5	1.23
	BS	83.9	6.9	1.6	7.7	0.98
6	HS	87.2	9.4	—	3.4	1.29
	BS	76.8	6.6	1.3	15.4	1.03

a) By difference.

The major separation was between the aromatic (9.20—6.00 ppm) and aliphatic (5.00—0.20 ppm) hydrogen resonances; the aliphatic region was further divided into six subgroups because the aliphatic region of the spectrum gave highly characteristic structural data regarding coal-derived products.[9)] The chemical shift of the phenolic OH proton was variable and its resonance was observed at between 8.50—4.00 ppm. The contribution of phenolic OH was small and made little difference in both the trends and conclusions deduced from the analytical data reported here. However, where applicable, we have subtracted its contribution based on an examination of the D_2O addition.

Tables 5 and 6 show the hydrogen distribution per 100 carbon atoms and the average structural parameters of HS and BS from Morwell and Taiheiyo coals, respectively. For a comparison, Table 7 gives the analytical data of HS and BS derived from the hydroliquefaction of Wandoan coal,[2)] among which all the data of BS and hydrogen distribution data of HS have not been previously reported. Important structural differences between the products from catalytic and noncatalytic runs (Tables 5—7) are cited as follows. The HS fractions of noncatalytic runs of Morwell and Taiheiyo as well as Wandoan coals have the highest $H_{\alpha2}$, $H_{\beta2}$, H_γ (except Morwell coal), and

Table 4. Assignments of Bands in ^{1}H NMR Spectra of HS and BS

Chemical shift δ (ppm from TMS)	Symbol	Assignments of hydrogen type
9.20—6.00	H_{ar}	Aromatics
5.00—3.40	H_F	CH_2 α to two aromatic rings
3.40—2.35	$H_{\alpha1}$	CH_2 α to an aromatic ring
2.35—2.00	$H_{\alpha2}$	CH_3 α to an aromatic ring
2.00—1.60	$H_{\beta1}$	CH_2 β to an aromatic ring
1.60—1.05	$H_{\beta2}$	CH_3 β to an aromatic ring CH_2 γ or further from an aromatic ring
1.05—0.20	H_γ	CH_3 γ or further from an aromatic ring

Tabe 5. Hydrogen Distribution and Structural Parameters of HS and BS from Morwell Coal

Run No.	Product	Hydrogen distribution per 100 carbon atoms							Structural parameters[a)]		
		H_{ar}	H_F	$H_{\alpha1}$	$H_{\alpha2}$	$H_{\beta1}$	$H_{\beta2}$	H_γ	f_a	σ	H_{aru}/C_{ar}
1	HS	29.4	2.1	23.4	15.5	7.9	35.5	11.2	0.57	0.38	0.84
	BS	31.9	6.5	16.2	5.6	4.5	22.0	7.3	0.71	0.29	0.64
2	HS	25.6	5.0	24.6	12.0	10.1	29.9	12.8	0.58	0.41	0.81
	BS	28.4	5.4	17.8	7.2	8.0	16.9	7.3	0.71	0.33	0.60
3	HS	27.8	6.2	26.5	11.3	9.4	26.6	11.2	0.58	0.42	0.82
	BS	27.1	4.4	18.2	8.0	8.6	15.9	9.8	0.71	0.34	0.58

a) f_a: aromaticity; σ: degree of substitution in aromatic systems; H_{aru}/C_{ar}: ratio of the number of aromatic hydrogen atoms to the number of aromatic carbon atoms for a hypothetical unsubstituted aromatic system.

Table 6. Hydrogen Distribution and Structural Parameters of HS and BS from Taiheiyo Coal

Run No.	Product	Hydrogen distribution per 100 carbon atoms							Structural parameters		
		H_{ar}	H_F	$H_{\alpha 1}$	$H_{\alpha 2}$	$H_{\beta 1}$	$H_{\beta 2}$	H_γ	f_a	σ	H_{aru}/C_{ar}
4	HS	21.5	1.1	19.2	13.3	8.0	57.7	22.2	0.45	0.40	0.80
	BS	29.3	6.6	20.1	5.8	6.1	18.2	7.9	0.70	0.34	0.64
5	HS	24.1	2.8	21.5	10.2	9.9	38.8	15.7	0.55	0.39	0.73
	BS	21.2	5.1	13.2	5.1	8.1	30.5	14.8	0.65	0.34	0.50
6	HS	22.4	2.8	23.7	11.4	10.7	41.9	16.1	0.51	0.43	0.77
	BS	21.9	7.0	18.9	8.0	9.9	26.2	11.1	0.63	0.42	0.60

Table 7. Hydrogen Distribution and Structural Parameters of HS and BS from Wandoan Coal

Run No.[a)]	Product	Hydrogen distribution per 100 carbon atoms							Structural parameters		
		H_{ar}	H_F	$H_{\alpha 1}$	$H_{\alpha 2}$	$H_{\beta 1}$	$H_{\beta 2}$	H_γ	f_a	σ	H_{aru}/C_{ar}
7	HS	21.3	3.8	21.0	11.0	8.5	57.9	20.5	0.44	0.45	0.88
	BS	26.8	6.1	19.4	9.7	7.1	36.1	9.8	0.59	0.37	0.73
8	HS	25.9	4.3	24.1	9.2	10.0	35.8	12.7	0.54	0.40	0.82
	BS	25.2	4.2	17.0	6.7	8.3	16.5	7.1	0.72	0.34	0.53
9	HS	24.7	4.4	24.7	9.8	11.3	38.1	14.0	0.53	0.42	0.81
	BS	23.0	7.7	16.9	7.4	10.1	20.1	10.8	0.67	0.39	0.57

a) Catalyst: run 7, none; run 8, $NiCl_2$-LiCl-KCl; run 9, $MoCl_3$-LiCl-KCl.

H_{aru}/C_{ar} values. The values of H_F, $H_{\alpha 1}$, $H_{\beta 1}$ and f_a of HS from the catalytic runs are higher than those of HS from noncatalytic runs.

A somewhat surprising observation is that the trends of differences in hydrogen distribution between the HS of noncatalytic and catalytic runs were quite clear and were the same for the three kinds of coals, regardless of the different nature of the coals (Tables 5—7). Generally, a BS showed a higher f_a value and lower $H_{\alpha'\beta'\gamma'}$, σ and H_{aru}/C_{ar} values than its corresponding HS. The values of H_{ar} and H_{aru}/C_{ar} of BS from catalytic runs were lower than those of the BS from noncatalytic runs, the $H_{\beta 1}$ value of the former being higher than that of the latter.

Discussion

Catalytic Effects of $MoCl_3$- and $NiCl_2$-LiCl-KCl Molten Salts. In direct coal hydroliquefaction, the initial step is a thermal fragmentation (depolymerization) of coal organic materials to produce large quantities of fragments which are extremely reactive.[13—14)] A thermogravimetric examination (in N_2) of the coal impregnated with catalysts indicated that the $MoCl_3$ and $NiCl_2$ catalysts effectively enhanced the initial thermal fragmentation of the coal.[2)] The coal-derived reactive fragments must be stabilized by the hydrogen of the coal, itself, through an autogeneous hydrogen-transfer mechanism[14)] and by the hydrogen from such external hydrogen sources as a hydrogen-donor solvent and/or gas-phase hydrogen; otherwise, they would promptly recombine or repolymerize to form insoluble organic materials.[14—16)]

It has been commonly recognized that in this stabilizing step, molecular hydrogen is much less effective than a hydrogen donor solvent such as tetralin.[17)] Taking our reaction conditions into consideration, the considerably decreased PyI yield of catalytic runs (Fig. 1) and our previous results[2,18—23)] suggest that in the initial reaction stage the molten-salt catalysts not only promote coal depolymerization but also act to reduce repolymerization by stabilizing the reactive fragments and permitting them to be capped by gas-phase hydrogen.

After the initial fragmentation and stabilization steps, these salts function as hydrocracking catalysts[2)] for the hydrocracking of stabilized heavy products such as PyS and BS. As shown in Table 2 and Fig. 1, for each run of the two coals, the increasing extent of the HS yield with the catalysts is much higher than that of conversion. Therefore, the high H_2 consumption during catalytic runs (Table 2) is probably mainly associated with the hydrocracking of PyS and BS to give a light HS product. These results reinforced our previous conclusion[2)] derived from results with Wandoan subbituminous coal: the $MoCl_3$ and $NiCl_2$ catalysts have a high hydrocracking ability and also show a high catalytic activity and HS selectivity.

It should be noted that the selectivity of a coal-liquefaction catalyst is probably more important than its activity.[1)] The high HS selectivity of the new catalysts is both of scientific and practical interest since HS is the most desirable oil product of coal hydroliquefaction.

Characteristics of Catalysis by $MoCl_3$- and $NiCl_2$-LiCl-KCl Molten Salts. It has been indicated[24)] that the best procedure for characterizing catalytic effects during coal liquefaction is to pay maximum attention to the liquid-oil part (HS) of the coal products. Yoshida et al.[25] have concluded that during the hydroliquefaction of coal, a cleavage of its ether bonds mainly contributes to the formation of PyS (preasphaltene); however the scission of CH_2 bridges and some naphthenic CH_2 bonds mainly contributes to the formation of HS (oil). As shown in Tables 5—7, ^{1}H NMR analysis indicated that among all the HS of catalytic and noncatalytic runs, HS of noncatalytic runs of the three coals had the lowest content of hydrogens α to two aromatic rings (H_F). This might be due to a cleavage of the ring-joining methylene bridges ($Ar-CH_2-Ar$), being consistent with highest content of methyl hydrogens in α-CH_3 ($Ar-CH_3$) ($H_{\alpha 2}$) of HS of noncatalytic runs. Moreover, the fact that the HS of noncatalytic runs has the highest amounts of hydrogens in β-CH_3 and γ-CH_2 ($H_{\beta 2}$) and γ-CH_3 (H_γ) together with its highest content of hydrogens in α-CH_3 ($H_{\alpha 2}$) suggests that many bridge structures like $Ar-(CH_2)_n-Ar$ ($n \geq 2$) which are rich in coal[26–27] and some naphthenic CH_2 bonds which are thermally sensitive,[25–26] have been cleavaged.

Interestingly, all the HS of catalytic runs had an even higher content of hydrogens in CH_2 α to two aromatic rings (H_F) than those of noncatalytic runs (Tables 5—7). Probably this was mainly the result of an increase of CH_2 hydrogen existing in structures like 9,10-dihydroanthracene and fluorene types. This is because the formation of these type compounds is reasonable[9] and their CH_2 hydrogens also resonate in the region of H_F.[8–9] Secondly, all the HS of catalytic runs contain larger amounts of hydrogens in α-CH_2 ($H_{\alpha 1}$) and β-CH_2 ($H_{\beta 1}$) than all of the HS of noncatalytic runs, indicating an increase in CH_2 hydrogens in hydroaromatic structures such as 9,10-dihydrophenanthrene,[9] tetralin and indan types.[12] With regard to the high HS yield, these results suggest that large amounts of polynuclear aromatic structures of the heavy products from these coals were considerably hydrocracked into relatively smaller hydroaromatic and aromatic structures as well as some alkyl aromatic structures, which accounts for the high activity of the catalysts.

Furthermore, all the HS of the catalytic runs contained smaller amounts of hydrogens in β-CH_3 and γ-CH_2 ($H_{\beta 2}$) and in γ-CH_3 (H_γ)(except Morwell coal) and showed higher f_a and lower H_{aru}/C_{ar} values than those of noncatalytic runs. These results, together with the relatively low yield of C_1–C_4 hydrocarbons of the catalytic runs, suggest that most of the newly formed smaller hydroaromatic and aromatic structures did not undergo much further ring-opening reactions. Therefore, the detailed structural study of HS has rationalized the high HS selectivity and activity of the $MoCl_3$ and the $NiCl_2$ catalysts.

It can be seen from Tables 5—7 that the structural differences between the BS of catalytic and noncatalytic runs are not as clear as those observed in HS. This suggests that the structural features of HS can not be directly correlated with those of BS, presumably because HS might also be formed directly from the thermal cracking and hydrocracking of BS and PyS as well as the coal.[28] Nevertheless, all the BS from catalytic runs contained smaller amounts of H_{ar}, larger amounts of $H_{\beta 1}$ and show a lower H_{aru}/C_{ar} value than all the BS of noncatalytic runs. This suggests that the relatively larger polynuclear aromatic compounds contained in coal and PyS were converted into BS by using the catalysts.

Through the present study, we have established the effectiveness of $MoCl_3$–LiCl–KCl and $NiCl_2$–LiCl–KCl molten salt catalysts for the hydroliquefaction of subbituminous and brown coals (especially subbituminous coals). Also, the characteristics of hydroliquefaction catalysis of these new catalysts was clarified. We believe that the analytical methods presented in this paper are useful in characterizing the catalytic effects of a catalyst for the hydrocracking of coal and coal-related materials.

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