Catalytic Upgrading of SRC from Pyrolytic Coal Liquefaction and Hydrocracking of Polycyclic Aromatic Hydrocarbons

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(Received April 21, 1988)

Synopsis. Catalytic upgrading of SRC (solvent refined coal) derived from short contact time pyrolytic liquefaction of Wandoan subbituminous coal was carried out. The upgrading with unsulfided and sulfided nickel-molybdenum catalysts produced about 77 wt% and 85 wt% of oil plus light distillates from the SRC, respectively. The reactions occurring during the upgrading process were assessed by referring to the hydrocraking of related polycyclic aromatic hydrocarbons.

The upgrading of various coal-derived products has been the subject of much research work concerning the second stage of two- or multi-stage coal conversions.[1-3] Recently, we have found that when relatively low heating rates are used, subbituminous coal can be efficiently converted into THF-soluble products in high conversions (85—88 wt%, daf) by pyrolytic procedures in an N_2-tetralin system under high temperature and short contact time conditions.[4] The present work was conducted in order to evaluate the extent of convertibility of the pyrolytically derived SRC by upgrading over supported nickel-molybdenum catalysts. Hydrocracking of some related polycyclic aromatic hydrocarbons over the same catalysts was also carried out for assessing reactions occurring during the upgrading process.

Experimental

The SRC (Table 1) used in this work was prepared by short contact time pyrolytic liquefaction of Wandoan subbituminous coal.[4] The polycyclic aromatics used in hydrocracking reactions were reagent-grade anthracene, phenanthrene, and bibenzyl. The catalysts examined were $NiO-MoO_3/Al_2O_3$ (NiMo) catalyst (Ketjenfine 153S: NiO, 2.9 wt%; MoO_3, 15.8 wt%; surface area, 255 $m^2 g^{-1}$; pore volume, 0.56 ml g^{-1}) and the corresponding sulfided catalyst (S-NiMo). The upgrading was carried out at 425 °C for 1 h with 4.9 MPa H_2 in a 70-ml SUS-316 rocking autoclave with SRC (2.5 g, −32 mesh), tetralin (5 g) and a catalyst (1 g, −100 mesh) together with a small stainless-steel ball. The products were separated into gas, light distillates (LD, C_5-250 °C), oil (hexane-soluble), asphaltene (benzene-soluble), and preasphaltene (benzene insoluble). Hydrocracking of polycyclic aromatic hydrocarbons was carried out at 400 °C for 1 h with 9.8 MPa H_2 in the autoclave with a given reactant (3 g) and a catalyst (0.3 g, −100 mesh). The products were analyzed by GC and GC-MS. Experimental details concerning this work are similar to those described elsewhere.[4-6]

Results and Discussion

The results of catalytic upgrading of the SRC are shown in Fig. 1. The short-contact-time pyrolytically derived SRC showed a relatively high reactivity toward upgrading, and about 10 wt% of LD and 59 wt% of oil was obtained in the noncatalytic run (Run 1), without any consumption of gas-phase H_2. The use of a NiMo catalyst and the corresponding S-NiMo catalyst improved the conversion of preasphaltene and asphaltene to oil and LD, increased the consumption of H_2 and decreased the net hydrogen transfer from tetralin, as can be seen from Fig. 1. Relative to a noncatalytic run, the yield of LD rose from about 10 wt% to 18 wt% with a NiMo catalyst (Run 2), and to 23 wt% with a S-NiMo catalyst (Run 3). The total yields of light product, oil+LD+gas, were 87.8 wt% with S-NiMo, 80.0 wt% with NiMo and 70.9 wt% without catalyst. These results indicate the high extent of convertibility of the SRC. S-NiMo showed a higher catalytic activity than NiMo for the upgrading; such a trend was also observed in runs with asphaltene.[7]

Table 2 gives elemental analysis and structural parameters of oil products, and Fig. 2 shows the gel permeation chromatograms of oil products. As compared to a noncatalytic run, the use of NiMo and

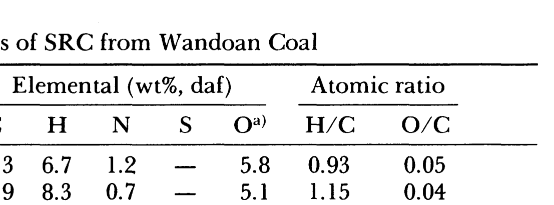


Fig. 1. Catalytic upgrading of SRC from short contact time pyrolytic liquefaction of Wandoan coal.

Table 1. Representative Analyses of SRC from Wandoan Coal

	Content (wt%, daf)			Elemental (wt%, daf)					Atomic ratio	
	Oil	Asp.	Preasp.	C	H	N	S	O[a]	H/C	O/C
SRC	31.3	23.3	13.5	86.3	6.7	1.2	—	5.8	0.93	0.05
Oil[b]	31.3	—	—	85.9	8.3	0.7	—	5.1	1.15	0.04
Asphaltene[c]	—	23.3	—	85.5	6.4	1.4	—	6.7	0.89	0.06
Preasphaltene[d]	—	—	13.5	85.6	4.9	1.6	—	7.9	0.68	0.07
Wandoan coal	0.9	4.7	1.7	78.3	5.9	1.0	0.1	14.7	0.90	0.14

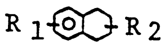
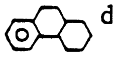
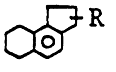
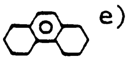
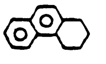
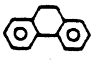
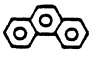
a) By difference; b—d) Hexane-soluble (b), hexane-insoluble but benzene-soluble (c), and benzene-insoluble but THF-soluble (d) portions of the SRC.

Table 2. Elemental Analysis and Structural Parameters of Oil Products

Run No.	Catalyst	Elemental (wt%) C	H	N	O[b]	Atomic H/C	Parameters[a] f_a	σ	H_{aru}/C_{ar}
1	None	85.7	7.7	0.9	5.7	1.07	0.64	0.34	0.67
2	$NiO-MoO_3/Al_2O_3$	88.6	8.1	0.8	2.5	1.10	0.61	0.37	0.68
3	$S-NiMo/Al_2O_3$	88.8	8.3	0.7	2.2	1.12	0.59	0.39	0.67

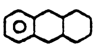
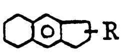
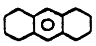
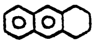
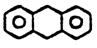
a) Calculated from ^{1}H NMR and elemental analytical data using Brown-Ladner equations. f_a: ratio of number of aromatic carbons to total carbons (aromaticity); σ: degree of substitution in aromatic systems; H_{aru}/C_{ar}: ratio of number of aromatic hydrogens to number of aromatic carbons for a hypothetical unsubstituted aromatic system. b) By difference.

Table 3. Hydrocraking of Phenanthrene

Run No. Catalyst	4 None	5 NiMo[a]	6 S-NiMo[b]
Products[c] (wt%)			
C_1—C_4	—	—	0.3
C_5—C_9	0.2	0.3	0.4
	0.1	1.0	2.0
	0.4	2.5	4.6
 [d] + 	—	13.5	15.6
 [e]	—	38.9	37.6
	0.8	11.0	8.4
	1.3	10.9	8.4
	96.3	19.8	18.3
Others	0.9	2.1	4.4
Conversion	3.7	80.2	81.7

a) $NiO-MoO_3/Al_2O_3$. b) $S-NiMo/Al_2O_3$. c) R, R_1, and R_2 mean alkyl groups or hydrogen. d) *unsym*-Octahydrophenanthrene. e) *sym*-Octahydrophenanthene.

Table 4. Hydrocracking of Anthracene

Run No. Catalyst	7 None	8 NiMo[a]	9 S-NiMo[b]
Products[c] (wt%)			
C_1—C_4	0.1	0.2	0.6
C_5—C_9	—	0.5	0.1
	—	—	0.4
	0.1	14.0	18.1
 [d] + 	0.3	17.4	21.5
 [e]	—	64.5	56.4
	14.9	2.9	2.3
	69.3	—	—
	14.4	—	—
Others	0.9	0.5	0.6
Conversion	85.6	100.0	100.0

a) $NiO-MoO_3/Al_2O_3$. b) $S-NiMo/Al_2O_3$. c) R, R_1, and R_2 mean alkyl groups or hydrogen. d) *unsym*-Octahydroanthracene. e) *sym*-Octahydroanthracene.

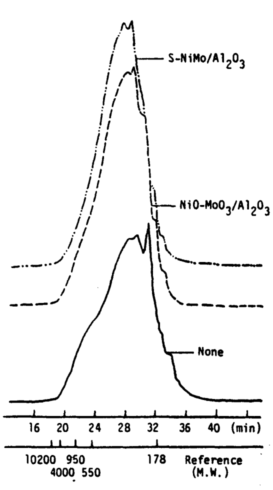


Fig. 2. Gel permeation chromatograms of oil products from catalytic upgrading (column, Shodex AC-801+AC-802; mobile phase, $CHCl_3$, 1 ml min^{-1}; UV detector, set at 254 nm).

S-NiMo facilitated a decreasing heteroatom content and aromaticity (f_a), and an increased atomic H/C ratio and the substitution extent of aromatics (σ) of oil products (Table 2), which correspond to the shift of the molecular size distribution of oil products of catalytic runs relative to a noncatalytic run toward the higher molecular size side (Fig. 2).

In order to assess the reactions occurring during the upgrading process, the hydrocracking of polyaromatics was carried out. The results in Tables 3 and 4 show that NiMo and S-NiMo significantly promoted hydrocracking reactions of phenanthrene and anthracene, whereas in the absence of catalyst a very limited amount of phenanthrene was converted (Table 3, Run 4) and anthracene was mainly converted into dihydroanthracene (Table 4, Run 7). Phenanthrene is known to have a low reactivity toward hydrogenation, and the major hydrogenated products of the catalytic runs are dihydro-, tetrahydro-, octahydrophenanthrene (Table 3). Anthracene showed much a higher reactivity, and in the catalytic runs, most of the intermediate hydrogenation products, such as dihydro- and tetrahydroanthracene, were converted into octahydroanthracene and hydrocracked products (Table 4). The major hydrocracked products are monocyclic and bicyclic hydrocarbons. Both in runs involving phenanthrene and anthracene, S-NiMo afforded higher yields of hydrocracked products than NiMo, indicating a higher activity of the sulfided catalyst than the unsulfided one (Tables 3 and 4). In the reaction of bibenzyl, S-NiMo and NiMo also promoted conversion of the reactant to 1-cyclohexyl-2-phenylethane and 1,2-dicyclohexylethane, but the yields of hydrocracked products, such as benzene, toluene, and ethylbenzene, were only slightly higher than those of a noncatalytic run.

The above results provided a basis for assessing the hydrocracking reactions of aromatic compounds present in SRC during the upgrading process. Most of the hydrocracked products shown in Tables 3 and 4, if formed from catalytic upgrading of the SRC, would fall into the category of light distillates. On the other hand, fairly larger amounts of the products from catalytic runs (Tables 3 and 4) are hydrogenation products, which did not undergo hydrocracking (ring-opening) reactions. Therefore, apart from hydrocracking reactions, it is possible that some of the polyaromatic substances present in heavy portions of the SRC were converted into oil products by hydrogenation reactions, since an increase in naphthenic rings in asphaltene and preasphaltene can also increase their solubility in hexane.[8] This would rationalize the shift of the molecular size distribution of oil products from catalytic runs toward the higher molecular size side (Fig. 2). The SRC, of course, contains a significant percentage of heteroatom-containing compounds (heteroatom content, Table 1); their adsorption and reactions on the catalyst surface would also take place and they may partly interfere with those of aromatic compounds.[9] As can be seen from Table 2, the most considerable decrease of oxygen content of oil from catalytic runs relative to that of noncatalytic run suggests that the major reactions of heteroatom-containing compounds that occurred during the upgrading process were hydrodeoxygenation reactions. It seems that hydrodeoxygenation is easier than hydrodenitrogenation.[10]

The combination of results regarding upgrading of the SRC (Fig. 1), the hydrocracking of pure hydrocarbons (Tables 3 and 4) and the analytical results of oil products from upgrading (Table 2, Fig. 2) strongly suggest that NiMo and S-NiMo catalysts promoted hydrogenation and cracking of polyaromatic substances present in heavy portions of the SRC and, thus, enhanced their conversion to oil and light distillates. Hydrogenation reactions, such as those shown in Tables 3 and 4, decreased the aromaticity (f_a, Table 2), and hydrocracking-derived alkyl aromatics contributed to the increase of substitution extent (σ) of oil products. These reactions were simultaneously accompanied by heteroatom removal, mainly hydrodeoxygenation reactions. However, as estimated from the H_{aru}/C_{ar} values shown in Table 2, the remaining aromatic compounds in oil products after the catalytic upgrading, have (on the average) similar ring sizes as those contained in oil from a noncatalytic run.

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