

HYDROCRACKING OF LIAOHE VACUUM RESIDUE WITH BIMETALLIC OIL-SOLUBLE CATALYSTS

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ABSTRACT

Hydrocracking of Liaohe vacuum residue was investigated in an autoclave promoted by oil-soluble molybdenum dithiocarbonylate, nickel and iron naphthenates as well as their mixtures. The reaction was conducted at temperature of 430°C, residence time of 1 hour, catalyst concentration of 200ppm(based on metal in feed), and initial hydrogen pressure of 7.0MPa. It was found experimentally that high residue conversion, and low coke(toluene insoluble) and light gas yields were achieved in the presence of the mixed catalysts, indicating the mixed catalysts to be more active than the single one for the hydrocracking of vacuum residue. It was also discovered that the synergism was obviously present for the bimetallic catalysts when the weight ratio of molybdenum to nickel or iron was 3 to 2. X-ray diffraction(XRD) analyses of the toluene insolubles indicated that the active species of catalysts were non-stoichiometric metal sulfides, and no joint sulfides occurred in the presence of bimetallic catalysts. Microscopy and transmission electron microscopy(TEM) analyses further revealed that the dispersion of catalysts was improved in the presence of the second metal.

KEY WORDS: Hydrocracking, Bimetallic Oil-soluble Catalyst, Vacuum Residue

INTRODUCTION

The use of homogeneous oil-soluble metal compounds to enhance the liquid yield and to reduce coke formation has been explored extensively in the hydrocracking of heavy feedstocks. These compounds are based on transition metals, such as Mo, W, Co, Ni, V, and Fe[1]. It is well known and of great industrial importance that the addition of a second transition metal such as Co or Ni to a binary sulfide such as MoS₂ or WS₂ can give rise to an enhancement of HDS activity. In this paper we investigated the application of bimetallic oil-soluble catalysts and evaluated the relative activities of these homogeneous catalysts for liquid phase catalytic hydrocracking of Liaohe vacuum residue.

It is generally accepted that Mo-based catalysts give the best performances in terms of coke inhibition and product upgrading. On the other hand, Fe-based materials are often used in slurry processes because of their lower cost even though they show very low activity toward hydrogenation reactions.

The degree of dispersion of the catalyst strongly affects its activity. Although high levels of catalyst dispersion can be achieved by introducing some techniques[2,3,4], adding oil-soluble catalyst precursors seems the best way to promote a good dispersion. A systematic investigation showed that catalyst performances are almost independent of the organic group bonded to the metal as long as the organic group has provided oil solubility as well as the thermal lability to the precursor[5].

It is clear that the most promising new catalysts might stem from research on promoted or multicomponent systems. The objective of the present investigation was to develop bimetallic oil-soluble catalysts and to evaluate the relative activities of these homogeneous catalysts. The aim was to determine whether sufficiently small quantities of these catalysts could be used so that they would not need to be recovered after hydrocracking. The objective was to accelerate the rate of the hydrogenation reactions to permit them to keep pace with thermal cracking of the asphaltene and thus yield more stable distillates.

EXPERIMENTAL

The hydrogenation reactions were performed on a vacuum residue (500+) of Liaohe crude with bimetallic oil-soluble compounds as catalyst precursors. The vacuum residue feedstock used throughout the experiments was Liaohe Tuozili vacuum residue supplied by the Liaohe Petrochemical Refinery. The properties of this feedstock were reported in Table 1. These catalysts were mixtures of molybdenum dithiocarboxylate (MoDTC) and nickel or iron naphthenate (NiNaph or FeNaph) which was prepared from the commercially-available precursors. The weight ratio of the two metals varied from 1:4 to 4:1.

The hydrocracking experiments were all conducted with 35g Liaohe vacuum residue in a 100mL magnetically-stirred autoclave equipped with a thermocouple well. The weight of metal catalyst was calculated to give 200 ppm of metal based on the vacuum residue feed. The catalyst was weighed and added directly to the residue in the autoclave without vehicle or solvent. Then little elemental sulfur was added to promote the generation of the active form of the catalyst. Next, the autoclave was sealed, purged of air, and the hydrogen pressure brought up to 7.0MPa. The autoclave temperature was brought up to 300°C at a heating rate of 13°C min⁻¹ and held at that temperature for half an hour to sulphidize the catalyst. Then the temperature was brought up to the reaction temperature of 430°C and holds for an hour.

After reaction the final autoclave pressure was measured and the autoclave was then cooled to room temperature. The gases in the autoclave were slowly vented to the fumehood and the autoclave was opened to permit the removal of the hydrocracked liquid product. The liquid products of the reactions were directly pumped into a weighed sample bottle and distilled using a modified ASTM D1160 procedure. Three distillate fractions were collected over three atmospheric boiling point ranges: initial boiling point (IBP) to 200°C, 200-350°C, 350-500°C and a residue of 500+°C.

Duplicate autoclave experiments were performed for the characterization the percentage yields of the coke (toluene-insoluble). The coke was then characterized in terms of elemental analysis, x-ray diffraction (XRD) analysis and transmission electron microscopy (TEM) analysis.

RESULTS AND DISCUSSION

Influence of Catalysts on Yield and Product Distribution

In order to obtain a preliminary indication of the effect of the bimetallic catalysts, we carried out several experiments with one oil-soluble catalyst. All experiments with one or two oil-soluble catalysts and the results were shown in Table 2 and Table 3. Runs 1, 7 and 13 were processes with one oil-soluble catalyst Mo, Ni and Fe. Others were processes with two catalysts of different metal ratios. The yields of coke and hydrocarbon gas reflect the activity of the catalyst. In general the changes in the two criteria associated with the changes of the organic portion of the catalyst were relatively minor. So from these two criteria it appears that the metals gave the following order of activity: Mo symbol 62 < "Symbol" \s 12> Ni symbol 62 < "Symbol" \s 12> Fe.

When the mixture of two oil-soluble catalysts was used, the yields of coke and light gas were lower than either the nickel naphthenate or iron naphthenate was employed alone under the same hydrocracking operating conditions. The conversion of the residue (the yield of the distillates 500°C-) were higher than the molybdenum dithiocarboxylate was employed alone. Especially when the weight ratio of molybdenum to nickel or iron was 3 to 2, the yields of coke and gas were the lowest. A comparison on the basis of the percentage yield of coke of the performance of the bimetallic oil-soluble catalysts suggests that the activity of the catalysts of this ratio was approximately the equivalent to that of the molybdenum dithiocarboxylate and superior to that of nickel or iron naphthenate.

Characterization of Catalysts

Solids (coke + catalyst) obtained from hydroconversion were characterized by several

techniques. At first, the x-ray diffraction data showed no evidence for the formation of a Ni-Mo (or Fe-Mo) sulfide. The two metals give rise to separate non-stoichiometric sulfides that may act as supplementary catalytic materials. Two metals bonded together, however, could produce a significantly modified Mo structure. When the ratio of the two metals was 3 to 2, the synergism was obvious.

From transmission electron microscopy (TEM) analysis, it appears that catalyst particles appear as irregular clusters of lamellas with a mean thickness of about 2-7nm (Figure 1). The size of the particles and irregular clusters in the presence of the bimetallic catalyst was smaller than that of the single-metal catalyst. This showed the dispersion of the promoted system was improved.

The microscopy analysis of the hydrocracked liquid phase verified previous conclusion (Figure 2). The very fine materials maybe catalyst particles absorbed with hydrocracked distillates. The mean size of the fine materials of the promoted system was much lower than that of the single-metal system. This indicated that the presence of the second metal improved the dispersion of the catalysts.

CONCLUSIONS

The results of this work demonstrate that the nature of the catalyst metal in the oil-soluble catalyst played a very significant role in governing the yields of coke and gaseous as well as liquid products. On improving the amount of hydrogen transfer under hydrocracking conditions by the using of mixtures of two oil-soluble catalysts, the coke yield decreased greatly. The bimetallic oil-soluble catalysts were superior in terms of residue conversion, as well as yield of coke and light gas, as compared to the use of single-metal catalysts. The synergism was especially obvious when the weight ratio of molybdenum to nickel or iron was 3 to 2.

X-ray analysis showed that, under the hydrocracking conditions, there is no evidence for the formation of a Ni-Mo (or Fe-Mo) sulfide. The synergism must stem from other causes. One reason maybe the improvement of the dispersion of the catalysts that was verified by TEM and microscopy analysis.

Promoted or multicomponent catalysts have excellent potential. If the concentration of the expensive metals can be decreased to an extremely low level, there is no necessary to recover the metals. However, further work is required to confirm these observations in a scaled-up operation. Additionally, it will be more advantageous to use the less expensive metal such as cobalt or nickel instead of the molybdenum for hydrocracking.

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Table 1.
Liaohu 500°C Vacuum Residue Feed

Density(20°C)	0.9976	C,%	86.9
Viscosity(100°C),cSt	3380	H,%	11.0
CCR,%	19.0	S,%	0.4
SARA analysis,%		N,%	1.1
saturate	17.4	Ni,ppm	123
aromatic	30.3	V,ppm	2.9
resin	50.2	Fe,ppm	38
Asphaltene(n-C7)	2.1	Ca,ppm	96

Table 2.
Effect of the Mo/Ni Catalysts on Products and Distribution

Run No. Ni/(Mo+Ni)	1	2	3	4	5	6	7
%Gas	5.4	5.6	4.8	5.4	6.0	6.7	6.5
%Coke	1.7	1.8	1.5	1.7	1.7	1.9	2.9
IBP-200°C(%)	5.3	3.0	3.4	3.4	4.4	3.1	6.6
200-350°C(%)	17.3	15.3	16.0	17.5	16.1	17.0	18.8
350-500°C(%)	28.5	27.0	26.9	27.4	28.3	28.7	26.1
500°C+(%)	41.8	47.3	47.4	44.6	43.5	42.6	39.1
Coke Quality							
H/C (at)	0.64	0.64	0.66	0.67	0.68	0.67	0.65
%N	3.5	3.3	3.2	3.5	3.5	3.4	3.5

Table 3.
Effect of the Mo/Fe Catalysts on Products and Distribution

Run No. Fe/(Mo+Fe)	1	8	9	10	11	12	13
%Gas	5.4	5.6	5.8	6.2	7.0	7.1	10.0
%Coke	1.7	2.0	1.7	2.9	3.0	3.3	7.1
IBP-200°C(%)	5.3	5.1	5.6	5.9	6.1	7.1	7.3
200-350°C(%)	17.3	17.1	18.4	18.6	20.3	21.9	23.7
350-500°C(%)	28.5	28.8	26.7	28.1	27.2	25.4	28.4
500°C+(%)	41.8	41.4	41.8	38.3	36.4	35.2	23.5
Coke Quality							
H/C (at)	0.64	0.66	0.64	0.65	0.68	0.67	0.65
%N	3.5	3.5	3.3	3.5	3.3	3.2	3.5

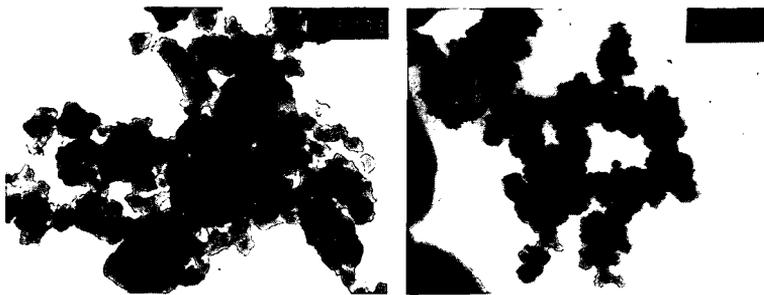


Figure 1. TEM micrograph of the solid obtained from Mo/Fe system (Mo:Fe=3:2, Magnification is $\times 19,000$ and $\times 100,000$ for left and right, respectively.)

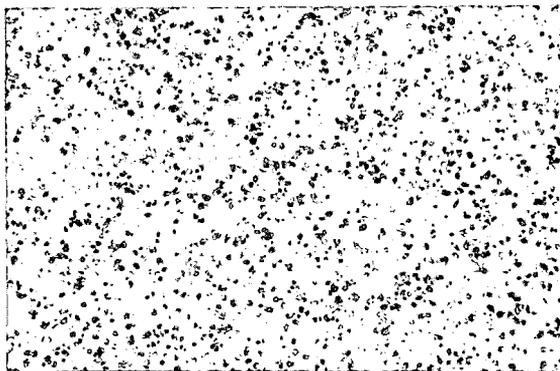


Figure 2. Micrograph of the hydrocracked liquid with Mo/Fe catalyst(Mo:Fe=3:2)