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Slurry-phase Residue Hydrocracking with Dispersed Nickel Catalyst

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Dispersed nickel catalysts were prepared by decomposition of an oil-soluble nickel compound precursor in residue. Effects of these catalysts on residue conversion and coke formation were investigated in an autoclave simulating slurry-phase residue hydrocracking. The results of this study demonstrate the following: as the catalyst's concentration increased, the yield of coke and light oil (Nap + AGO) decreased; as the reaction pressure increase, the yield of coke decreased but the yield of light oil increased; and as the reaction temperature increased, coke formation and light oil increases. The dispersed catalysts used for the slurry phase hydrocracking were separated from the feedstock and were analyzed by X-ray diffraction and scanning electron microscopy. The results showed that the active catalytic species of dispersed catalyst was the mixture of hexagonal NiS (JCPDS 120041), millerite NiS (JCPDS 431469), and cubic Ni_3S_4 (JCPDS 431469); its particle size was about 1−5 μm.

1. Introduction

Slurry-phase residue hydrocracking is a newly developed technique for processing heavy oils.[1−3] Slurry-phase residue hydrocracking using dispersed catalysts is based on thermal reactions of the heavy molecules that decompose to unstable fragments and free radicals.[4]The function of dispersed catalysts is to reduced solids formation in the reactor and to remove heteroatoms.[2,5]Catalysts for slurry-phase hydrocracking of heavy oil has undergone two development phases, that is, heterogeneous solid powder catalyst [6−9] and homogeneous dispersed catalysts.[10−16]The homogeneous dispersed catalysts are divided into water-soluble dispersed catalyst and oil-soluble dispersed catalyst. Solid powder catalyst have low catalytic activity, which will produce a large number of solid particles in bottom oil; thus, it is difficult to dispose and utilize. Dispersed catalyst is highly dispersed and has a greater surface area to volume ratio. Therefore, it shows high catalytic activity and good performances. It is a desirable catalyst for slurry phase hydrocracking of heavy oil. Water-soluble catalysts have inhibited coke effect, are priced cheaply, and have been studied by several literates.[14−16] Most of the dispersed catalysts need to be presulfurized to sulfides with high catalytic activity.[15,17] During water-soluble catalyst sulfurized procession, it lots of water is taken into the feedstock, which then needs stirring for a specific time; the feed oil was heated to 140 °C and bubbled with nitrogen to remove the water.[15] This process consumes a large amount of energy.

The oil-soluble catalyst precursors are well-dispersed in residue and have high activity. Therefore, oil-soluble metal precursor as catalysts have become popular. Dispersed catalyst decomposed by oil-soluble catalyst precursor is favored in the hydrogenation reactions and also interfers with the coalescence of the mesophase.[18,19] The chemical nature, the catalytic activity, and the cost of these catalysts are the key factors for the optimization and development of efficient hydrocracking processes.[20] In this paper, a cheap, oil-soluble nickel compound precursor was mixed with the feedstock, and the precursor was generated into active species of catalysts by thermal decomposition. The catalyst effects on product yields and product quality was studied for slurry-phased residue hydrocracking.

2. Experimental Section

2.1. Raw Material and Catalysts. LiaoHe atmospheric residue (LHAR) was taken as feedstock for the hydrocracking reaction. The typical characteristics of LHAR are shown in Table 1. The structure of the catalyst precursor used for the reaction was shown in Figure 1.

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Table 1. Properties of LHAR

density at 20 °C (g/cm^3)	1.0064
viscosity at 100 °C (mm^2/s)	1443.56
CCR (wt %)	16.32
C7-asphaltene (wt %)	4.19
elemental analysis (wt %)	
C	86.57
H	11.00
N	0.86
S	0.45
nickel (μg/g)	118
calcium (μg/g)	552
vanadium (μg/g)	2.6

In Figure 1, A is an aromatic ring system containing 6 carbon atoms; R is an independent hydrocarbyl group containing 12 carbon atoms; n is at least 1 and may equal the number of positions available for substitution in A; and X is an independent linker group. The nickel compound is an amphipathic molecule primarily consisting of two active parts; an adsorbing part (ring system A), which sticks to the surface of the asphaltene particle and which carries a long chain (R) attached to the ring. A is a aromatic, largely flat molecule whose ring gives sufficient interactions through van der Waal's forces to attach itself to the similarly aromatic asphaltene.

2.2. Steps of the Experiment. The hydrocracking reaction was conducted in batch mode using a 500 mL autoclave. The feedstock was prepared by directly mixing the desired concentration of nickel catalyst precursor with feedstock, and elemental sulfur was taken as a sulfurized reagent. In a typical experiment, the reactor was charged with 150 g of feedstock, pressurized with hydrogen, and heated to the reaction temperature. After 60 min, the reactor was cooled with water to cease the hydro-reaction.

The products are leached, and the solids are extracted with hot toluene to obtain the toluene-insoluble products, that is, the coke, which is dried and weighed; the filtrate liquor is distilled to get the naphtha fraction (<180 °C), atmospheric gas oil (180−350 °C), and residue (>350 °C). (The amount of coke was calculated by subtracting the weight of the catalyst from the residue.) The amount of gas was calculated by subtracting the weight of the liquid and solid products from the residue.

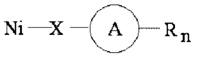


Figure 1. The structure sketch map of catalyst precursor

Table 2. Results of Different Reaction Conditions

reaction	coke/wt%	gas/wt%	nap./wt%	AGO/wt%	residue/wt%
thermal cracking	10.43	7.59	14.24	27.76	39.52
hydrocracking[a]	1.31	2.15	10.99	29.31	56.20

[a] With 300 μg/g dispersed Ni catalyst.

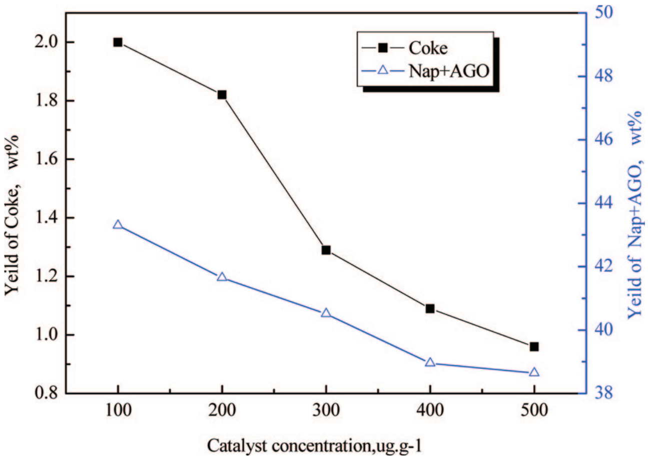


Figure 2. Effect of catalyst concentration on distillate fractions yields (6.0 MPa of hydrogen, 425 °C, and reaction time of 1 h).

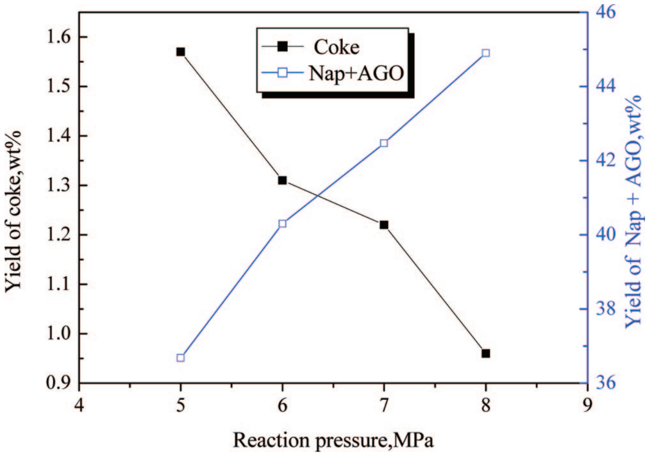


Figure 3. Effect of hydrogen initial pressure on distillate fractions yields (catalyst concentration: 300 μg/g, 425 °C, and reaction time of 1 h).

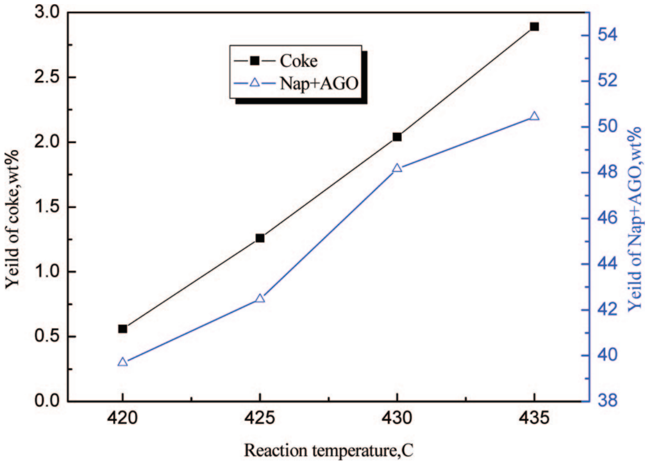


Figure 4. Effect of reaction temperature on distillate fractions yields (catalyst concentration: 300 μg/g, hydrogen pressure: 7.0 MPa, and reaction time 1 h).

Table 3. Elements Analysis Results of LHAR and Coke

sample	C%	H%	H/C ratio	Ni/ppm
LHAR	86.57	11.00	1.51	118
coke	87.50	4.10	0.56	21400

The objective of this work was to evaluate the effect of catalyst concentration and hydrogen pressure and reaction temperature on product yields and quality. The experiments were carried out by varying these three parameters within a wide range (0−500 μg/g of nickel dispersed catalyst, 5−8 MPa of initial hydrogen, and 420−435 °C reaction temperature), at different levels of reaction severity.

2.3. Characterization of Catalysts. The X-ray diffraction (XRD) data were collected using a D/MAX-IIIA diffractometer, Cu Ka radiation (D1.54178 Å). Scanning electron microscopy (SEM) was done using a DEL-1200EX transmission electron microscope; the samples for SEM analysis were prepared by dispersing the filtered, dry powder of catalyst in toluene. Elemental analyses were carried on the elemental analysis equipment (Varil EL-3) and on an atomic absorption spectroscometer (Hitachi Z800).

3. Results and Discussion

3.1. Reaction Parameter Analysis. First compare the thermal reaction and slurry phase hydrocracking reaction results at the reaction temperature of 425 °C, initial hydrogen pressure of 6.0 MPa, and reaction time of 1 h, shown in Table 2.

As Table 1 shows, the viscosity of LHAR is large, the CCR is high and the metal content is high, thus it is difficult to

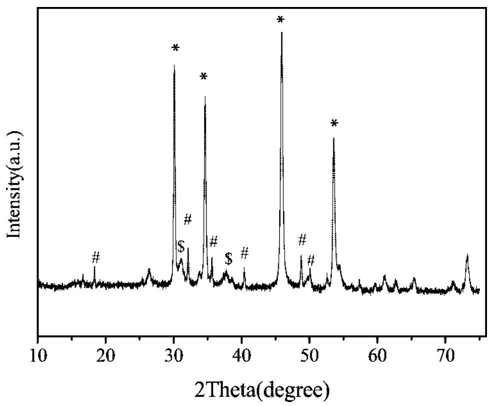


Figure 5. XRD spectra of catalyst, ∗, hexagonal NiS (JCPDS 120041); #, millerite NiS (JCPDS 431469); $, cubic Ni_3S_4 (JCPDS 431469).

process. From Table 2 we can see that thermal cracking was able to produce a lighter fraction and more residue conversion than catalytic hydrocracking, but the yield of coke was 10.43%, significantly greater than hydrocracking's 1.31%; thus, the catalyst was obviously inhibiting the coke formation and also inhibited the residue cracking reaction. This result agrees with ref 9. The reason could be that dispersed catalysts do not contain acidic functions, so that the reactions involving C−C bond cleavage are thermally controlled; the catalyst only provides a hydrogen uptake, which controls the free radicals evolution, thereby inhibiting both condensation and cracking reactions.

Figures 1−3 show the trends of distillate fractions and coke formation as a function of catalyst concentration and hydrogen pressure.

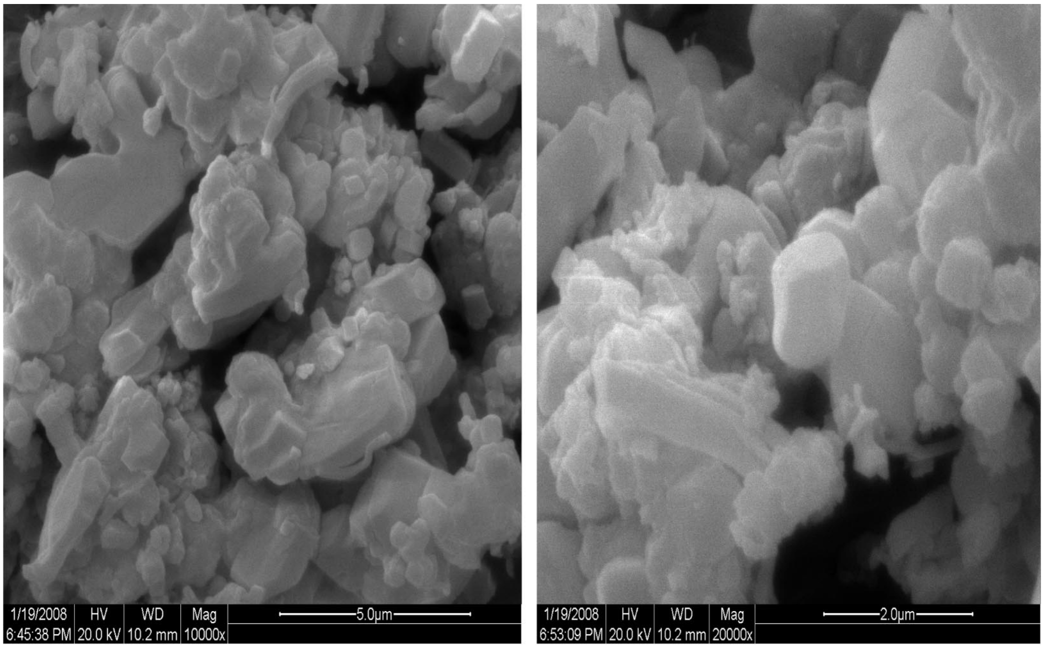
As can be seen in Figure 2, as the catalyst's concentration increased, the yield of coke and light oil (Nap +AGO) decreased. According to ref 5, solids formation (coke) would be reduced by capping radical intermediates with hydrogen under the hydrocracking reaction. Reference 14 had studied the water-soluble dispersed catalyst on residue slurry-phase hydrocracking. From the results, during the slurry phase of heavy oil hydrocracking, the catalyst reacts on the feedstock and the H free-radical is formed on the surface of the catalyst. The H free-radical formed on the surface of the catalyst could react with the free-radical of big molecules, thereby restraining the formation of coke during the reaction.

The positive effect of higher catalyst concentration is reduced coke formation but, at the same time, the liquid yields were negatively affected. Thus, the choice of an appropriate catalyst concentration is very important.

As can be seen from Figure 3, the yield of coke decreased with the increasing of reaction pressure, but the yield of light oil increased. The heavy oils hydroprocessing studies by Ancheyta et al. determined that high partial pressure of hydrogen is desirable to decrease the rate of coke formation.[21] Ünchez and Ancheyta[22] studied the effect of pressure on the kinetics of the hydrocracking under mild operating conditions. They found that higher pressure and lower space velocity led to higher conversion. The increase in pressure will help not only the yield of light oil but also the saturation and hydrocracking of aromatic molecules, and it will prevent catalyst deactivation due to coke formation.

Figure 4 shows that the yield of light oil and coke increases as the reaction temperature is increased. This is because, while in the higher range of temperatures, a cracking reaction mechanism maybe plays a significant role, in which the feed molecules disappear to form gas-oil, middle distillates, naphtha, gas, and coke. As the operating temperature rises, the cracking severity increases, resulting in subsequent cracking of gas-oil into middle distillates, naphtha, gas, and coke. When the temperature was higher, the cracking reaction was fiercer, and the yield of coke and the gas-oil ratio were higher. However, this may accelerate the deactivation of the catalyst, which needs to be taken care of by increasing hydrogen pressure.

From the previous data we can determine that the dispersed catalyst could inhibit the coke formation under high hydrogen pressure. To study the catalysts' effect more completely, elemental analysis, SEM, and XRD analyses were carried out.



(a) (b)

Figure 6. SEM photos of dispersed Ni Catalysts. Magnification: (a) 10000× and (b) 20000×.

3.2. Elemental Analysis of LHAR and Reaction Coke. The elemental analysis of LHAR and the coke yield by slurry phase hydrocracking reaction are shown in Table 3.

Table 3 shows us elemental compositions of LHAR and the coke. The coke's H content (wt %) and H/C atom ratio are obviously reduced, which explains that the aromatics contained in the residue had the dehydrogenation and the condensation reaction. At the same time, the nickel element was also concentrated in the coke, which may come from catalyst that was trapped by the coke during reaction.

The presulfurized catalysts were recovered with hot toluene in the residue before the reaction happened. The catalysts were examined by XRD and SEM.

3.3. XRD Analysis of Catalysts. The catalysts were characterized by the XRD analysis; the results are shown in Figure 5.

The reflection peaks in Figure 5 can be easily indexed as the mixture of hexagonal NiS (JCPDS 120041), millerite NiS (JCPDS 431469), and cubic Ni_3S_4 (JCPDS 431469). These kinds of crystalline granules of catalysts could well be responsible for converting hydrogen to the H free-radical,[14]hence terminating the chain reactions which lead to coke formation, and according to Lott et al.,[23] the metal sulfide particle accumulate on the surfaces of coke spheroids and interfere with coke precursor coalescence.

3.3. SEM Analysis of Catalyst. From Figure 6 we can see that the dispersed Ni catalysts accumulated separately. The surface is smooth, and the Ni catalysts show either hexagonal or cubic-like shape with diameters of about 1−5 μm. A higher magnification of as-prepared transition-metal sulfide is shown in Figure 6b, which offers a clearer view of the surface morphology. Under relatively high magnification, some small nanocrystals can be seen on the sphere surface, which make the sphere surface appear rough, and indicates that these small nanocrystals are composed of the microsphere compounds.

4. Conclusions

On the basis of the results of our study, the results derived from the hydrocracking of LHAR residue in the presence of dispersed nickel can be summarized as follows:

(1) The conversion of the feedstock to distillate is thermally controlled and is practically independent of catalyst concentration and hydrogen pressure; as the catalyst's concentration increased, the yield of coke and light oil (Nap + AGO) decreased; as the reaction pressure increased, the yield of coke decreased but the yield of light oil increased; and as the reaction temperature increased, coke formation and light oil increased.

(2) For the catalysts analyzed by XRD and SEM, the results showed that the active catalytic species of dispersed catalyst was metal sulfide; its particle size was about 1−5 μm.

(3) The sulfide catalyst in the reaction could restrain the formation of coke.

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