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Role of Catalyst in Hydrocracking of Heavy Oil

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The relative contributions of the catalytic reaction and thermal cracking in the hydrocracking of heavy oil were evaluated in detail. It is concluded that light oil fractions are formed mainly by thermal cracking and the main role of the catalyst is to supply hydrogen to the heavy oil fraction and prevent its carbonization. The behavior of sulfur and nitrogen in hydrocracking without a catalyst was clarified. Sulfur transfers to both light and heavy fractions, but nitrogen transfers to asphaltene and the benzene-insoluble fraction and practically no nitrogen transfers to the light oil fraction.

INTRODUCTION

Hydrocracking is a process to hydrogenate and cleave the C–C bonds of hydrocarbons using hydrogen gas and a catalyst and thereby convert them into compounds of lower molecular weight. Its purpose is to obtain high-quality fuel oil or chemical substances of high added value from the heavy oil fractions of petroleum. Industrial hydrocracking processes presently employed include isocracking (*1*), unicracking-HJC (*2*), HDC Unibon (*3*), H-G hydrocracking (*4*), H-Oil (*5*), IFP-BASF hydrocracking (*6*), and LC-Fining (*7*). There still remain many technological difficulties and economic problems in direct hydrocracking of the residual oil, and in practice most of the above industrial processes employ distilled or pretreated heavy oil.

Available crude oil, on the other hand, becomes increasingly heavier worldwide; extraction of crude oil from oil shale or tarsand is also in the process of industrialization (*8*). Accordingly, the demand for direct hydrocracking of heavy oil has increased rapidly in recent years. Various oil fractions contain sulfur, nitrogen, oxygen, and metals; on combustion, the former two are discharged into air as SO_x and NO_x and thus are the sources for air pollution. With the increasing oil consumption in recent years, hydrotreating processes to remove these impurities have been developed rapidly. In Japan, however, the hydrotreating processes are operated to minimize the consumption of hydrogen gas and to suppress hydrocracking of heavy oil. Considering the high construction and operation costs and the increasing heaviness of crude oil, one expects that hydrocracking will be included, in the near future, in the hydrotreating process of heavy oil in order to produce chemical substances of high added value simultaneously with desulfurization and other treatments.

The present work was carried out from the above standpoint, and the basic factors involved in hydrocracking of heavy oil were examined in detail. Besides catalytic reactions, thermal reactions are known to occur to a significant extent in hydrocracking of heavy oil; however, their contribution has not been evaluated in detail. Since this point is important in the search for an effective catalyst, the emphasis of the present study was placed on it.

EXPERIMENTAL

Materials. The feedstock used was Khafji atmospheric residue; 3.98 wt% of sulfur, 0.25 wt% of nitrogen, 1.55 (atom/atom) of H/C ratio, and 10.6 wt% of asphaltene. Nickel-molybdenum/alumina catalyst (3.23 wt% NiO, 14.24 wt% MoO_3) was prepared by impregnating alumina (0.72 ml/g

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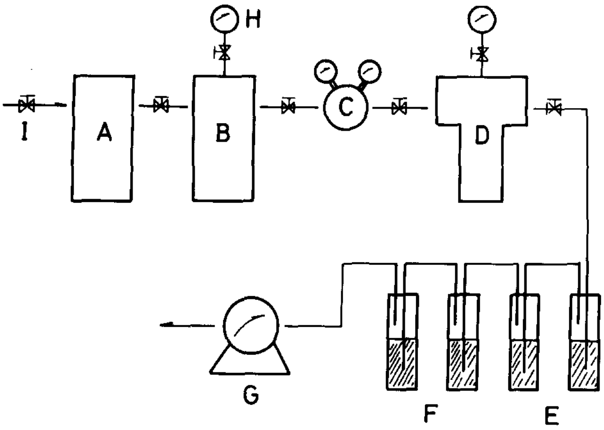

FIG. 1. Schematic diagram of reaction apparatus. (A) Compressor. (B) Gas holder. (C) Pressure controller. (D) Autoclave. (E) H_2SO_4 aq. trap. (F) KOH aq. trap. (G) Gas meter. (H) Pressure gauge.

pore volume and 227 m^2/g surface area) with a solution of ammonium paramolybdate and nickel nitrate. The impregnated material was extruded in pellets of 1.5 mm diameter and 5 mm length and was sulfided at 450°C for 2 h with a 10 : 1 mixture of H_2/H_2S after being calcined in air at 450°C for 24 h.

Apparatus and experimental procedure. Figure 1 is a schematic diagram of the autoclave system used in this study. The system was based on an autoclave engineers 300-cm^3 magnedrive reactor. Each run was operated at the following conditions: Feedstock, 100 g; Total pressure, 150 atm; Reaction period, 6 h; Catalyst (pellet), 10 g or none.

A typical experimental procedure was as follows. After replacement of the air in the reaction system with hydrogen gas, the autoclave was heated to 50°C and the hydrogen pressure was boosted to 65 atm under agitation. Then the autoclave was heated to 400°C and the hydrogen pressure was raised to 150 atm. The reaction was performed at 400°C for 6 h. During the reaction the total pressure was maintained at 150 atm by use of pressure controller C.

Analytical method. Figure 2 shows the analytical procedure for the oil. After the reaction had been completed, the autoclave was cooled to 50°C and then its pressure was measured. The consumption of hydrogen gas was calculated from both the decrease of hydrogen pressure of gas holder B and the analytical results of gaseous products in the autoclave.

The gas produced in the autoclave was released at 50°C into the air through trap E containing 0.5 *N* sulfuric acid and trap F containing 1 *N* KOH. A part of the gaseous product was sampled before trap E and the composition was determined by gas chromatography. Since the gas composition was changed with purging, the sampling was repeated at intervals of 30 min and the volume of gas purged was measured by gas meter C. When the pressure was lowered down to the atmospheric pressure, new hydrogen gas was introduced from gas holder B and sampling and purging were continued for 24 h. After the purging, about 10% of the pentanes was estimated to remain in the autoclave. The amount and composition of gaseous hydrocarbon were calculated from the gas composition and sample volume.

After purging of the gaseous product, the liquid and solid product were taken out of the autoclave with a pipet and spoon. In the case of the catalyst being used, there was no solid substance other than the catalyst. Several sheets of facial tissue papers were

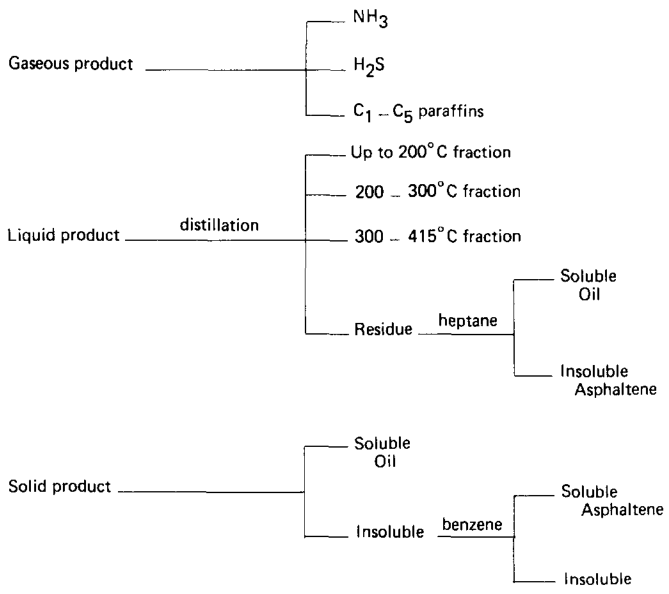

FIG. 2. Analytical procedure for the produced oil.

used to clean the autoclave and weighed. The yield of liquid product was compensated by adding the weight gained. The total product taken out of the autoclave was filtered to separate into liquid and solid components. The liquid component was distilled first at atmospheric pressure up to 200°C and then at a reduced pressure of 20 Torr up to 180 and 260°C. Each of the distilled fractions was weighed and analyzed by means of a Hewlett–Packard 5880 gas chromatograph with a SP-2100 capillary column (50 m × 0.2 mm). The chromatographic operating conditions are summarized in Table 1.

The distilled residue (vacuum bottoms) was separated into a heptane-soluble fraction (oil) and a heptane-insoluble fraction (asphaltene) in a Soxhlet extractor. No significant amount of benzene-insoluble fraction was obtained from the heptane-insoluble fraction.

The solid component was separated into a heptane-soluble fraction and a heptane-insoluble fraction which was further separated into benzene-soluble and benzene-insoluble fractions. Each of the heptane-soluble and benzene-soluble fractions was very small in quantity and was added to the oil and asphaltene fractions, respectively. In the case when the catalyst

TABLE 1

Chromatographic Operating Conditions

Detector		Flame ionization, Nitrogen-phosphorous detector
Detector temperature		240°C
Sample injector temperature		260°C
Column	SP-2100	50 m long, 0.2 mm in diameter, fused silica coated with dimethyl silicone fluid
	OV-1	50 m long, 0.2 mm in diameter, fused silica coated with dimethyl silicone gum
Liquid sample volume		1.0 μl
Split ratio		1/100
Initial temperature		50°C for 25 min
Program temperature		5°C/min 100°C for 5 min 3°C/min 150°C for 3 min 2.5°C/min
Final temperature		260°C held for 50 min

TABLE 2

Comparison of the Product Composition at 400°C

Product (wt%)	Catalyst		Feed
	With	Without	
C_1–C_5 paraffins	4.4	4.5	
Up to 200°C	12.3	12.4	
200–300°C	14.3	13.2	0.3
300–415°C	29.7	25.5	16.1
Oil	36.3	30.5	73.0
Asphaltene	1.1	7.2	10.6
Benzene insoluble	2.2[a]	4.1	
Loss[b]	1.3	4.0	
H_2 addition (mol/100g of feed)	0.83	0.20	

[a] Not coke precursor but compounds adsorbed strongly on the catalyst.

[b] Probably caused both by escape of C_6 or higher hydrocarbons during the gas purge and by remaining of the product in dead space of the autoclave system.

was used, the benzene-insoluble fraction was obtained as an increase in weight of the catalyst after the extraction procedure.

RESULTS

Hydrogen Consumption and Properties of Formed Oil

In order to examine the catalytic action in hydrocracking, comparisons were made between the oils formed in the presence and in the absence of the catalyst. In Table 2 the hydrogen gas consumption (moles per 100 g of feed) and the yield of various fractions (wt%) are shown. In the case where the catalyst was used, a benzene-insoluble fraction was obtained as the differential weight of the catalyst between the beginning and end of the reaction.

The consumption of hydrogen gas in the presence of the catalyst was found to be ca. four times larger than in the absence of the catalyst. The yields of gaseous hydrocarbons (C_1 to C_5) and light oil fractions of boiling points below 300°C, however, were found to be quite similar. The fractions in the range of 300–415°C as well as the heptane-soluble oil fraction, on the other hand, were obtained in larger quantities in the presence of the catalyst than in its absence; the noncatalytic cracking afforded a larger quantity of asphaltene, which is soluble in benzene, but insoluble in heptane, and gave a considerable amount of benzene-insoluble residue which was not present in the original oil.

The composition of each fraction, 415°C or below in boiling point, was analyzed with a gas chromatograph, and the contents of aromatics, linear paraffins, and other saturated hydrocarbons (branched paraffins and naphthenes) are listed in Table 3. No marked differences can be found between the catalytic and noncatalytic reaction as to the composition of each fraction. The use of the catalyst led to an increase in the yields of aromatics in the light fraction, and an increase in the yields of linear paraffins in the 300–415°C fraction. The composition of the gaseous fraction was essentially the same: 40.5 wt% methane, 18.5 wt% eth-

TABLE 3

Type Analysis of Distillate Fraction Obtained at 400°C

Yield (wt%)[a]	Catalyst	
	With	Without
Up to 200°C fraction		
Linear paraffins	3.0	3.1
Aromatics	3.9	2.0
Others	6.0	7.3
200–300°C fraction		
Linear paraffins	3.7	3.7
Aromatics	5.7	5.3
Others	5.0	4.2
300–415°C fraction		
Linear paraffins	12.7	9.2
Aromatics	14.1	14.2
Others	2.9	2.2
Total		
Linear paraffins	19.4	15.9
Aromatics	23.1	21.4
Others	13.8	13.7

[a] Calculated from % area of gas chromatogram.

TABLE 4

Comparison of H/C Ratio of the Product Obtained at 400°C

H/C Ratio (atom/atom)	Catalyst		Feed
	With	Without	
C_1–C_5 paraffins	3.19	3.19	
Up to 200°C fraction	1.77	1.89	
200–300°C fraction	1.69	1.74	
300–415°C fraction	1.71	1.64	1.71
Oil	1.63	1.42	1.54
Asphaltene	1.58	0.85	1.03
Benzene insoluble	1.17	0.57	

ane, 17.7 wt% propane, 3.1 wt% isobutane, 9.9 wt% butane, 3.9 wt% isopentane, and 6.4 wt% pentane. Olefins were found only in small quantities even in the noncatalytic reaction, the combined yield being less than 2 wt%. The partial pressure of hydrogen gas was 43 atm at 50°C after reaction, which indicates that it was ca. 90 atm at 400°C in the final period of the reaction. The combined pressure of other light compounds was then ca.60 atm which is estimated to be approximately twice as large as the partial pressure of methane.

In Table 4 are shown the H/C values of various fractions. The H/C value tends to decrease with increasing heaviness of the fraction, indicating that heavier fractions contain aromatics in larger amounts. Any fraction obtained by the catalytic reaction has a H/C value higher than that of the corresponding fraction of the original oil, indicating that hydrogenation is effected by the catalyst. The heavy oil fractions, 300°C or higher in boiling point, obtained by the noncatalytic reaction, on the other hand, have low H/C values; particularly, the H/C value of the benzene-insoluble fraction is only slightly above 1/2.

The yields of tetralin, naphthalene, methyltetralins, and methylnaphthalenes are shown in Table 5. When the catalyst was used, the yields of tetralin and methyltetralins were two to three times as large as those in the absence of the catalyst; the yields of naphthalene and methylnaphthalenes, on the other hand, decreased somewhat. The remarkable differences in the H/C values of the heavy oil fractions containing large contents of polycyclic aromatics, noted in Table 4, are explained as follows. In the catalytic reaction, polycyclic aromatics undergo partial hydrogenation and cleavage with hydrogen supplied by the catalytic action, while in the noncatalytic reaction hydrogen necessary for cracking is supplied by hydrogen abstraction from the heavy oil fraction. When the reaction is performed under high hydrogen pressures, the catalytic hydrogenation is accelerated considerably while noncatalytic hydrogenation to the hydrogen deficient heavy oil fraction, presumably promoted by metallic compounds contained in the heavy fraction, proceeds to some extent and the carbonization is partially suppressed.

While large differences in H/C value are noted with heavy oil fractions of boiling points above 300°C, the H/C values of light oil fractions obtained in the presence and in the absence of the catalyst do not differ greatly. Thus, the light oil fractions are likely to be formed by thermal cracking. Since the products are mostly paraffins, olefins being formed only in small quantities, it is suggested that hydrogen atoms are transferred from the heavy to light oil fraction as cracking proceeds.

TABLE 5

Composition of the Yield of Tetralins and Naphthalenes Obtained at 400°C

Yield (wt%)[a]	Catalyst	
	With	Without
Tetralin	0.41	0.19
Methyltetralins	1.00	0.33
Naphthalene	0.06	0.07
Methylnaphthalenes	0.36	0.48

[a] Calculated from % area of gas chromatogram.

TABLE 6

Comparison of the Material Balance of Hydrogen Obtained at 400°C

Hydrogen addition (mol/100 g of feed)	Catalyst	
	With	Without
Hydrodesulfurization	0.12	0.03
C_1–C_5 paraffins	0.18	0.18
Up to 200°C fraction	0.10	0.10
200–300°C fraction	0.08	0.08
300–415°C fraction	0.12	0.10
Oil	0.11	−0.15
Asphaltene	0.02	−0.05
Benzene insoluble	—	−0.08
Total	0.73	0.21
Average molecular weight		
Up to 200°C fraction	123	123
200–300°C fraction	178	165
300–415°C fraction	250	255

In Table 6 are shown the estimated hydrogen consumptions of various fractions. The amount of hydrogen consumed by desulfurization was estimated from the amount of H_2S formed. For the 415°C or lower fractions, the average molecular weight of each fraction was determined by gas chromatography/mass spectrometry, and 1 mol of molecular hydrogen was assumed to be consumed in producing each mole of hydrocarbon. As for fractions higher than 415°C, hydrogen addition or elimination was evaluated from the difference of the H/C values before and after cracking. The hydrogen balance obtained by the above rough approximation was found to agree well with the hydrogen consumption shown in Table 2. It is therefore suggested that in the absence of the catalyst the amount of hydrogen transferred from the heavier fraction (0.28 mol) is approximately 3/2 times that supplied from the gaseous phase (0.20 mol), while in the presence of the catalyst a quantity of hydrogen ca. 2 times as large as that needed for cracking and desulfurization (0.40 mol) is supplied from the gaseous phase (0.83 mol). The main role of the catalyst in the present reaction is therefore to supply hydrogen to the heavy oil fraction, which becomes deficient in hydrogen due to hydrogen abstraction, and thereby prevent its carbonization. The catalyst also hydrogenates polycyclic aromatics partially and thereby converts them into decomposable substances. The light oil fractions are thus suggested to be formed mainly by thermal reactions.

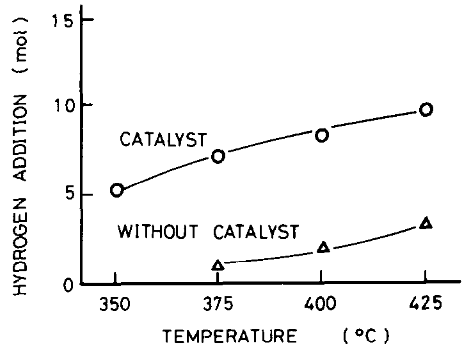

FIG. 3. The effect of temperature on the amount of hydrogen adsorbed.

In order to differentiate the catalytic and thermal reactions further, cracking was carried out in the temperature range of 350–425°C in the presence and in the absence of the catalyst. The dependence of the yield of each fraction on the reaction temperature is depicted in Figs. 3–6. As shown in Figs. 3

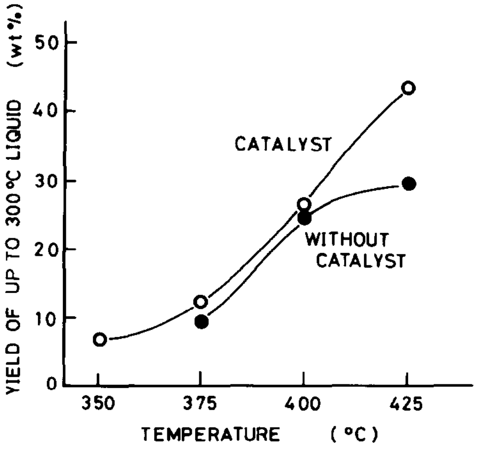

FIG. 4. The effect of temperature on the yield of liquid product under 300°C b.p.

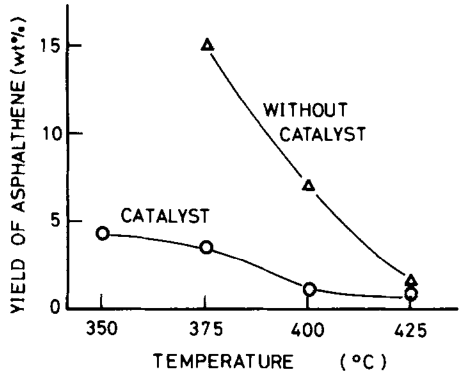

FIG. 5. The effect of temperature on the yield of the asphaltene fraction.

and 4, both the hydrogen consumption and the yield of the light oil fraction increase with increasing reaction temperature; the increase rate of the latter, however, is much faster than that of the former. The ratio of hydrogen supplied from the gaseous phase to that consumed by cracking thus appears to decrease with increasing reaction temperature, resulting in increased carbonization of the heavy oil fraction.

The yield of asphaltene decreases and that of the benzene-insoluble fraction increases with increasing temperature, as shown in Figs. 5 and 6. In Fig. 7 is shown the relationship between the H/C value of asphaltene and the reaction temperature; the H/C value decreases with increasing temperature. Thus, while acceleration of asphaltene decomposition at higher temperatures is clearly indicated by its decreasing yield, its heaviness increases at the same time. This, together with the increased yield of the benzene-insoluble fraction, suggests that decomposition of the heavy oil fraction into light oil fractions proceeds thermally and in a stepwise manner, but that other reactions leading to increased heaviness also proceed simultaneously and become pronounced at higher temperatures. This may be due to the fact that hydrogen cannot be supplied from the gaseous phase fast enough to compensate for hydrogen consumed by thermal cracking. The difference between the reactions in the presence and in the absence of the catalyst can be stated as follows. There is consecutive decomposition of the heavy oil fraction into light oil fractions and its carbonization in hydrocracking of the heavy oil; the former is dominant when the catalyst is used while the latter is dominant in the noncatalytic reaction. This inclination is accelerated at higher temperatures.

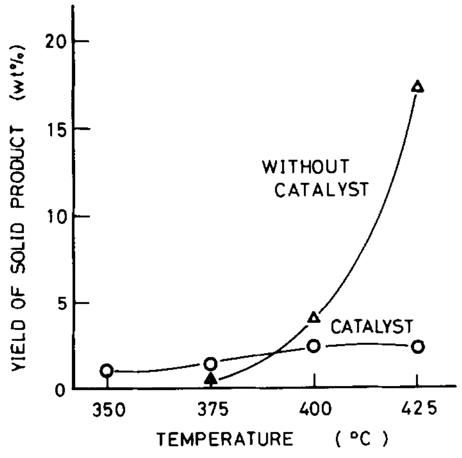

FIG. 6. The effect of temperature on the yield of benzene-insoluble fraction.

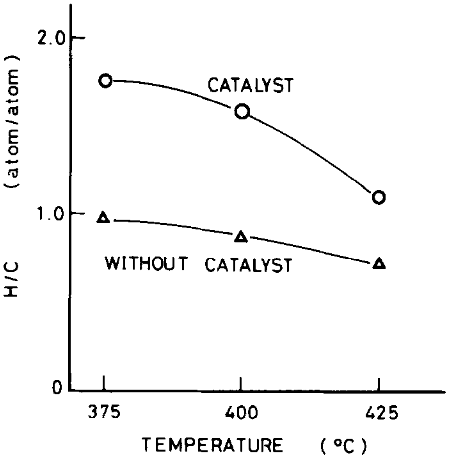

FIG. 7. H/C value of asphaltene fraction.

Hydrodesulfurization

The sulfur content of each fraction in weight percentage is shown in Table 7.

TABLE 7

Content of Sulfur

	Temperature (°C)							Feed
	With catalyst				Without catalyst			
	350	375	400	425	375	400	425	
Fraction	wt% of sulfur							
Up to 200°C	—	0.08	0.04	0.05	0.71	0.65	0.42	—
200–300°C	0.10	0.05	0.04	0.04	1.74	1.74	2.24	—
300–415°C	0.30	0.15	0.14	0.18	2.42	2.61	3.63	1.96
Oil	1.10	0.42	0.23	0.22	3.90	4.19	6.06	4.11
Asphaltene	2.02	1.21	0.72	0.39	6.35	6.30	4.90	6.11
Benzene insoluble					9.20	7.37	5.17	

When the catalyst is used, the sulfur contents are quite low; practically no sulfur is contained in fractions of 300°C or below. The sulfur content of the distillation residue, on the other hand, is relatively high in the case when the reaction is carried out at 350°C. When the reaction temperature is raised to 375°C or higher, however, it decreases to below 10% of the sulfur content of the corresponding fraction of the original oil. The catalytic removal of sulfur atoms is promoted at temperatures higher than 375°C. The sulfur content of the benzene-insoluble fraction could not be evaluated because of the catalyst having been presulfided. In the absence of the catalyst, the sulfur contents are generally high. Although the sulfur content decreases with increasing lightness of the fraction, even the fractions of 300°C or below in boiling point still contain more than 10 times as much sulfur content as those of the corresponding fractions obtained by the catalytic reaction.

The noncatalytic reaction carried out at 375°C gave benzene-insoluble fraction in a yield as low as 0.4%, but its sulfur content was found to be as high as 9.2%. As the reaction temperature was raised, the yield of the benzene-insoluble fraction increased, accompanied by a decrease in sulfur content. A similar trend is observed with the asphaltene fraction. With the lighter fraction, the sulfur contents increase with increasing reaction temperature.

The absolute quantity of sulfur contained in each fraction obtained by the noncatalytic reaction is given in Table 8. It is clearly indicated that sulfur is partitioned between the fractions heavier than asphaltene and the distillable fractions. The sulfur contained in the original oil probably resides both in the rings of polycyclic aromatics and in the ring-bridging chains and alkyl substituent groups; the former sulfur, after hydrogen transfer reactions, will be found in the benzene-insoluble fraction, while the latter sulfur will be transferred to the light oil fractions after thermal cracking. The sulfur contents of asphaltene and the benzene-insoluble fraction increase with de-

TABLE 8

Sulfur Distribution of the Products without Catalyst

	Temperature (°C)			Feed
	375	400	425	
	Amount of sulfur (g/100 g of feed)			
Up to 200°C	0.02	0.07	0.07	
200–300°C	0.11	0.23	0.30	
300–415°C	0.56	0.67	0.51	0.32
Oil	2.08	1.28	0.39	3.00
Asphaltene	0.73	0.45	0.09	0.65
Benzene insoluble	0.04	0.30	0.90	

TABLE 9

Content of Nitrogen

	Temperature (°C)							Feed
	With catalyst				Without catalyst			
	350	375	400	425	375	400	425	
Fraction				wt% of nitrogen				
300–415°C	0.02	0.05	0.04	0.10	0.03	0.05	0.13	0.03
Oil	0.15	0.15	0.16	0.29	0.17	0.23	0.33	0.22
Asphaltene	0.92	0.73	0.29	0.20	0.95	1.03	0.74	0.82
Benzene insoluble plus catalyst	0.44	0.49	0.49	0.45	1.16	1.26	0.86	—

creasing reaction temperature, while those of distillable fractions increase with increasing temperature. Therefore, compared with sulfur-free compounds, sulfur-containing compounds in general appear to discharge hydrogen atoms easily and resist decomposition. When the catalyst is used, decomposition of asphaltene is promoted. Hydrogenation and desulfurization, both consuming hydrogen of the gaseous phase, appear to promote the decomposition of the asphaltene fraction. It is concluded that sulfur-containing compounds are decomposed to some extent without catalyst while sulfur atoms are preferably removed in the presence of the catalyst.

Hydrodenitrification

Crude oil contains approximately 0.25 wt% of nitrogen atoms. The presence of nitrogen-containing compounds appears to affect the overall reactivity of crude oil, particularly that of its heavy oil fraction. The nitrogen content of each fraction in weight percentage is shown in Table 9. In the case where the catalyst was employed, nitrogen atoms in the benzene-insoluble fraction, which were not coke precursors but hydrocarbons strongly adsorbed on the catalyst surface, were inseparable from those trapped directly by the catalyst. Whether or not the catalyst is used, the nitrogen contents of the light oil fraction are extremely low. They do, however, increase with increasing reaction temperature, but the nitrogen contents in the heavy oil fractions decrease. In the case where the catalyst is employed, the nitrogen content of the asphaltene is lower, while that of the benzene-insoluble fraction is rather higher (2–5 wt%) supposing that nitrogen atoms are not trapped directly over the catalyst and considering that the benzene-insoluble fraction is 10–20% of the catalyst in weight. This suggests that some of the nitrogen atoms are trapped directly by the catalyst, presumably as NH_3 molecules.

When the catalyst is employed, denitrification appears to proceed, but most of the nitrogen removed from the oil formed, is found to be captured by the catalyst. At temperatures higher than 400°C, however, catalytic denitrification is found to proceed.

The nitrogen-containing compounds in the formed oil were detected selectively using a gas chromatograph equipped with a Nitrogen-phosphorous detector. In Fig. 8 are shown the chromatograms of nitrogen compounds contained in the 415°C or lower fractions of the oil formed at 400°C without the catalyst. Of the identified compounds, carbazole has the highest concentration. Most of the compounds are three- or higher-membered cyclic compounds with boiling points above 350°C. The concentrations of acridine and phenazine, commonly

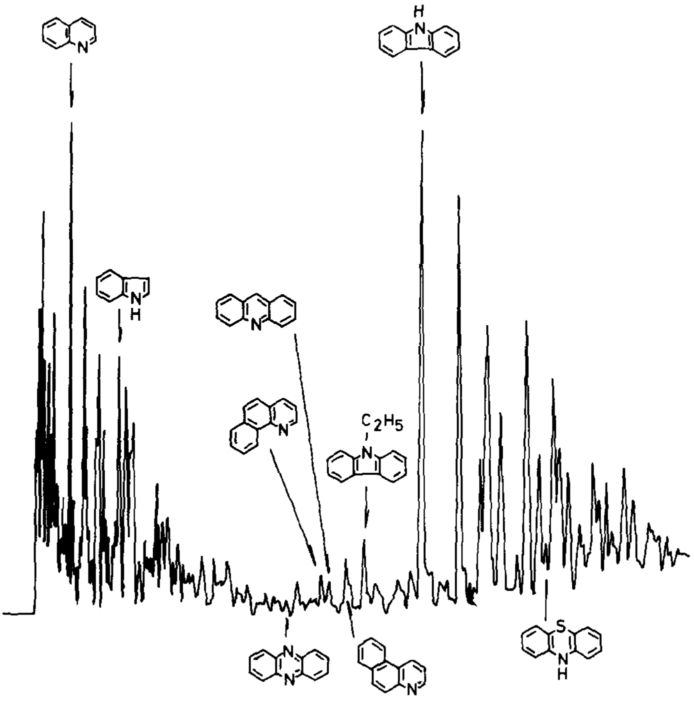

FIG. 8. Gas chromatograph analysis of N-compounds by Nitrogen-phosphorous detector.

identified products, were found to be rather low. With fractions of 300°C or higher, no significant differences are noted between the chromatograms of the oils obtained in the presence and in the absence of the catalyst.

In Fig. 9 is shown the chromatogram of the nitrogen compounds contained in small quantities in the 300°C or lower fraction. The presence of various pyridines and pyrroles is noted. The nitrogen content of this fraction is quite low; the concentration esti-

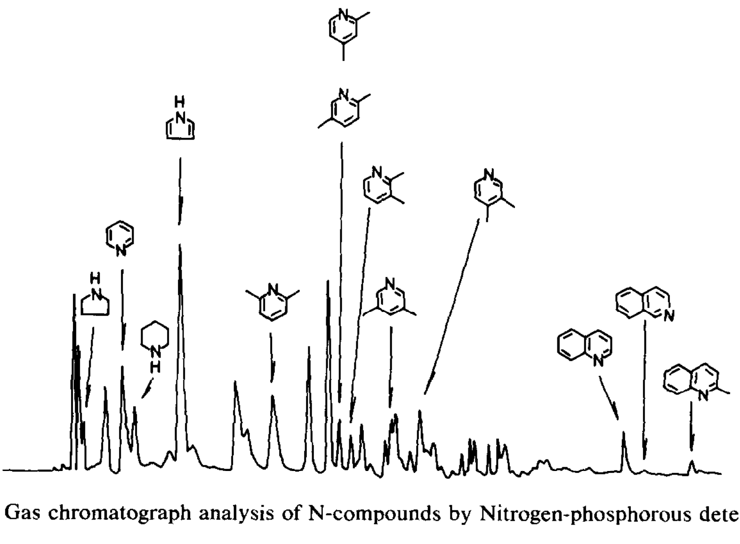

FIG. 9. Gas chromatograph analysis of N-compounds by Nitrogen-phosphorous detector.

mated from the chromatogram is 0.0001% for the catalytic reaction and 0.0005% for the noncatalytic reaction, both carried out at 400°C. Low-boiling-point compounds such as pyridines and pyrroles are thus found to be catalytically denitrified.

DISCUSSION

Our concern is the role played by the catalyst in the hydrocracking of heavy oil. According to a study on the hydrocracking of pure hydrocarbons of relatively low molecular weight (*9*), bifunctional catalysts having acidic sites as well as active sites for hydrogenation are effective catalysts; cracking proceeds mainly at the acidic sites of the catalyst, giving more branched paraffins than linear ones. Even with industrial hydrocracking processes employing distilled oils, such as isocracking (*1*) and H-G Hydrocracking (*4*), the ratio of isobutane to n-butane is generally high, suggesting that the acidic sites are involved in cracking.

It is generally believed that few industrial processes for hydrocracking residual oil have reached the stage of actual operation. This is not only due to economic reasons such as that related to hydrogen consumption, but also due to deterioration of the catalyst caused by deposition of carbonized or metallic substances. Visbreaking (*10*), a thermal cracking process for residual oil, employs an operation temperature of 430–480°C and total pressure of 20 atm maximum, which is relatively close to the temperature range used by hydrocracking processes, and reportedly produces mostly linear paraffins.

The main reaction involved in catalytic hydrocracking of heavy oil is said to be thermal cracking (*11–14*). The relative contributions of the catalytic reaction and thermal cracking, however, have not been evaluated in detail. The results of the present study indicate that the gaseous and light oil fractions of boiling points below 300°C have practically the same compositions, whether cracking is carried out in the presence or in the absence of the catalyst. These fractions are thus suggested to be formed mainly by thermal cracking, and to be desulfurized principally by virtue of the catalyst. The yield of linear paraffins in the 300–415°C fraction, on the other hand, increases when the catalyst is used. The decomposition products are believed to undergo radical polymerization in the absence of the catalyst and give heavy products. We believe that high-molecular-weight linear paraffins further undergo dehydrogenation/cyclization to give even heavier products. Furthermore, the use of the catalyst led to an increase in the yield of tetralins. Hydrogenation of naphthalenes or hydrogenation/ring opening of condensed polycyclic aromatics is likely to occur catalytically. Even for this fraction, however, the main reaction appears to be thermal cracking.

The yield, H/C value, sulfur content, and nitrogen content of each fraction of the distillation residue oil depend markedly on whether or not the catalyst is employed, indicating that the catalyst plays an important role in hydrogenation, decomposition, desulfurization, and denitrification of the heavy oil fraction. It appears that the main components of the heavy oil fraction, i.e., condensed polycyclic aromatics, undergo hydrogenation/ring-opening in the presence of the catalyst or dehydrogenation/polycondensation in the absence of the catalyst. Sulfur-containing compounds, on the other hand, are thermally cracked to give lighter products; the catalyst, however, is necessary to remove sulfur as H_2S. Nitrogen-containing compounds resist cracking or denitrification by thermal reactions, and thus after thermal cracking, nitrogen is concentrated in the asphaltene and benzene-insoluble fractions. When the catalyst is used, the nitrogen content of the distillation residue as well as the concentrations of pyrroles and pyridines in the distilled oil decrease; on the other hand, the concentrations of carbazole and other polycyclic nitrogen compounds do not change appreciably. Condensed polycyclic sulfur com-

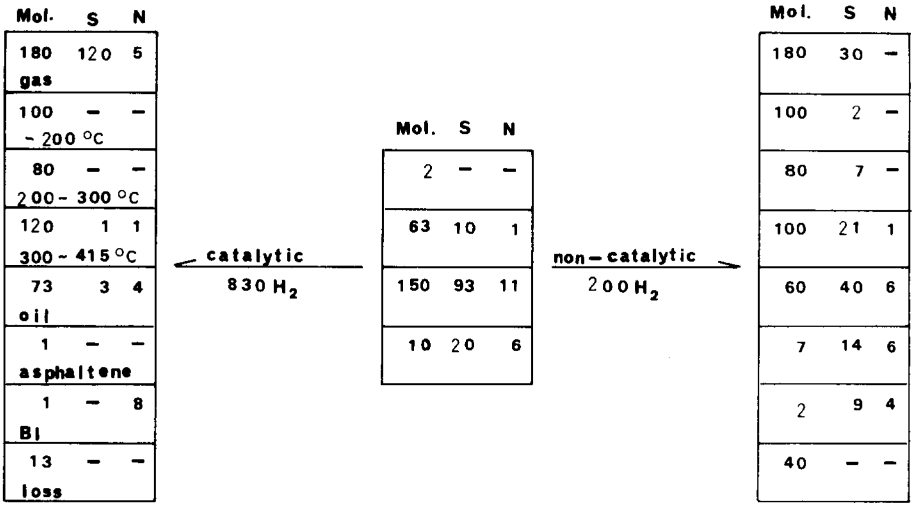

FIG. 10. A hypothetical scheme of the reaction using average molecular weight (at 400°C). The distribution of molecules, nitrogen atoms, and sulfur atoms. Average molecular weight: Loss, 100; oil, 500; asphaltene, 1000; benzene insoluble, 2000.

pounds are known to undergo desulfurization prior to hydrogenation of the ring adjacent to the sulfur-containing heteroring, whereas in the case of condensed polycyclic nitrogen compounds hydrogenation of the adjacent ring proceeds first, followed by denitrification (*15*). Condensed polycyclic compounds in the heavy oil undergo partial hydrogenation in the presence of the catalyst; complete hydrogenation, e.g., hydrogenation of tetralins to decalins, however, does not proceed easily. Thus, while monocyclic pyrroles and pyridines are decomposed catalytically, carbazole and other condensed polycyclic nitrogen compounds appear to resist decomposition. Denitrification of the distillation residue, however, is apparently promoted in the presence of the catalyst. The mechanism of denitrification involved is not clear; catalytic denitrification may occur, followed by thermal or catalytic decomposition, which leads to formation of light oil.

For the purpose of comprehending the total reaction visually, a hypothetical scheme of the reaction (at 400°C) combining hydrodesulfurization (HDS), hydrodenitrification (HDN), cracking and hydrogenation is presented in Fig. 10. In this scheme molecular weights of 100, 500, 1000, and 2000 are used as the average for loss, oil, asphaltene, and benzene-insoluble fractions. This scheme supposes a crude oil consists of 63 molecules of the 300–415°C fraction which contains 10 atoms of sulfur and 1 atom of nitrogen, 150 molecules of oil contain 93 atoms of sulfur and 11 atoms of nitrogen, and 10 molecules of asphaltene contain 20 atoms of sulfur and 6 atoms of nitrogen. In the case where the catalyst is used, the total number of molecules increases from 225 to 568, 120 atoms of sulfur and 5 atoms of nitrogen are removed and 830 mol of hydrogen are added, which indicate that during the reaction cracking occurs 343 times HDS 120 times, HDN 5 times, and hydrogenation 830 times. In the case of the noncatalytic reaction, on the other hand, cracking occurs 344 times, HDS 30 times, and hydrogenation 200 times, which indicates that 1/3 to 1/2 of the cracking occurs without accompanying hydrogenation. This is roughly in agreement with the previous discussion concerning Table 6.

According to our previous studies, sulfurized molybdena–alumina catalysts have acidic character (*16*) and catalytically de-

TABLE 10

Nitrogen Distribution of the Products

	Temperature (°C)							Feed
	With catalyst				Without catalyst			
	350	375	400	425	375	400	425	
	Amount of nitrogen (g/100 g of feed)							
300–415°C	—	0.01	0.01	0.02	0.01	0.02	0.02	0.01
Oil	0.09	0.08	0.06	0.03	0.09	0.08	0.02	0.16
Asphaltene	0.04	0.02	—	—	0.14	0.08	0.05	0.08
Benzene insoluble plus catalyst	0.10	0.11	0.11	0.10	—	0.05	0.14	
Total	0.23	0.22	0.18	0.15	0.24	0.23	0.23	0.25

compose, isomerize, and hydrogenate monocyclic aromatics (*17*), paraffins (*18*), and condensed polycyclic naphthenes (*19*). In the present study, however, we did not find marked catalytic effects on the cracking of heavy oil, except for desulfurization and denitrification. This is not only due to facile thermal decomposition of heavy oil under the conditions used, but also probably to deactivation of the acidic sites by adsorption of nitrogen compounds or condensed polycyclic aromatics. The active sites for hydrogenation are likely to be poisoned as well, making it difficult for secondary hydrogenation of light oil fractions, such as monocyclic aromatics, to proceed. In fact, hydrocarbons, whose weight corresponds to 20% of that of the catalyst, remain on the catalyst as benzene-insoluble material. Their H/C value is ca. 1, which is roughly equal to the H/C value of the asphaltene in the original oil, which might account for the above-mentioned partial deactivation of the Ni–Mo catalyst.

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