[Regular Paper]

Deactivation of Hydrodesulfurization Catalysts in Two-stage Resid Desulfurization Process (Part 5) Characterization of Asphaltenes after Hydrodemetallization and Subsequent Hydrodesulfurization Reactions

Hiroyuki SEKI^{†1)*}, Shinya SATO^{†2)}, and Masao YOSHIMOTO^{†1)}^{†1)} Advanced Catalysts Research Laboratory, Japan Petroleum Energy Center, KSP R&D 1237, 3-2-1 Sakado, Takatsu-ku, Kawasaki 213-0012, JAPAN^{†2)} National Institute for Resources and Environment, 16-3 Onogawa, Tsukuba, Ibaraki 305-5869, JAPAN

(Received August 3, 2000)

Hydrodemetallization (HDM) and subsequent hydrodesulfurization (HDS) of Arabian light (AL) atmospheric residues were performed with a bench-scale unit, and the structure of the asphaltenes obtained from each reaction was characterized. The HDM reaction caused a decrease in the number of aromatic rings, an increase in aromaticity, and a decrease in the number of alkyl side chains, but no formation of naphthenic rings. In contrast, HDS reaction formed naphthenic rings, but their number decreased with an increase of HDS temperature, thus leading to an increase of aromaticity. Using the structural parameters obtained by using a computer program based on the SAAH system developed by Katayama *et al.*, we modeled the structure of asphaltenes after HDM and HDS reactions and found that the aromatic unit structure of AL asphaltenes became coronene-type as hydrotreatings proceed.

1. Introduction

Petroleum asphaltene structure is of interest to many researchers because a further knowledge of its chemical structure is the key for understanding asphaltene behavior in thermal and catalytic processes in industry. Despite such interest, the structure of asphaltene has not been clarified since asphaltenes are a mixture of complex compounds. Therefore, determining the average structure of such complex materials is needed, and thus, average structures of asphaltenes have been reported^{1)–7)}. Yen *et al.* examined the asphaltene structure by using X-ray diffraction, and proposed an asphaltene skeleton^{1),2)} in which asphaltenes consist of polycondensed aromatic cores that have alkyl side chains. This proposed asphaltene structure is now widely accepted. Although there is still a debate about the size of aromatic cores, recent studies have reported that the aromatic core of asphaltene contains 5–10 benzene rings^{8)–12)}.

The average molecular weight (*MW*) is an important parameter in determining not only the macrostructure but also the aromatic core of asphaltene. In general, gel permeation chromatography (GPC) and vapor pressure osmometry have been used to determine *MW*. Colloidal properties of asphaltenes, however, some-

times hinder the determination of asphaltene *MW* with these two methods; for example, GPC is influenced by the measurement conditions such as temperature and type of solvent, and thus gives an asphaltene *MW* of higher than 10,000^{13),14)}. In contrast to these two methods, laser desorption mass spectrometry (LD-MS) is relatively unaffected by the asphaltene colloidal properties, and is therefore currently used to obtain asphaltene *MW*^{8),12),15)–18)}. Lazaro *et al.* performed a detailed study on the effects of instrument-related parameters (*e.g.*, laser power and ion-exchange voltage) on the mass spectra and concluded that LD-MS was the most suitable and reliable technique to determine *MW* of asphaltenes if measurement conditions were optimized¹⁷⁾. Moreover, another benefit of LD-MS measurements is a capability of obtaining information on the *MW* distribution.

In catalyst deactivation for resid hydrotreatings, asphaltene chemistry and behavior during hydroprocessing are important because asphaltenes act as coke precursors and deactivate hydrotreating catalysts^{19)–21)}. We have been studying the deactivation of HDS catalysts in two-stage resid desulfurization (RDS) processes, which consist of HDM and subsequent HDS processes^{22)–25)}. The following results were obtained; (i) the HDS catalysts are deactivated mainly by coke, (ii) asphaltene aromaticity (*fa*) is a good index of the catalyst deactivation, and (iii) asphaltene quantity

* To whom correspondence should be addressed.

affects the catalyst deactivation. Clarification of the structural changes of asphaltene, therefore, is needed to understand the HDS catalyst deactivation in two-stage RDS processes. Although structural changes of asphaltenes by either HDM reaction alone or reaction combined with HDM and HDS have been reported^{(7), (26) ~ (28)}, to our knowledge, asphaltene structural changes by each reaction, HDM and subsequent HDS, have not been reported.

In this study, we conducted HDM and HDS treatings and then, using LD-MS which gave a reliable *MW*, made structural characterization of asphaltenes obtained at each step in the HDM and HDS processes to understand the coke deactivation of HDS catalyst. Obtaining information on asphaltenes after HDM reaction is useful because asphaltenes in HDM product oil deactivate HDS catalysts, and that after HDS reaction is also important to know what kind of reaction takes place during HDS reaction. In addition, the average structure of asphaltenes for each reaction was proposed using the structural parameters obtained with SAAH method.

2. Experimental

2.1. Feed and Catalysts

Arabian light atmospheric residue (AL-AR) was used as feed of HDM reaction, containing 3.4 wt% sulfur and 3.0 wt% asphaltenes. **Table 1** lists other properties of the feed.

Some properties of the catalysts were summarized in **Table 2**. The HDM catalyst contained only MoO₃ (4.2 wt%) on an alumina support, and had a surface area of 200 m²/g, pore volume of 0.85 ml/g, and average pore diameter of 17 nm. The HDS catalyst contained MoO₃ (10.5 wt%), NiO (0.7 wt%), and CoO (1.2 wt%), and had a surface area of 211 m²/g, pore volume

of 0.64 ml/g, and average pore diameter of 12 nm. Both catalysts were used as received (1/22-inch extrudate).

2.2. HDM and HDS Reactions

A trickle bed flow reactor was used in the HDM reaction of AL-AR. First, the HDM catalyst (300 ml) was presulfided with a mixture of light gas oil and di-*t*-butyl-disulfide (total S = 3.0 wt%) at 300°C for 24 h. Then, the HDM reaction was carried out under the following conditions: 370-420°C, 14 MPa, LHSV 0.5 h⁻¹, and H₂/oil ratio 340 Nm³/kl.

A micro-flow reactor was used in the HDS reaction. The HDS catalyst (15 ml) was loaded in the reactor and the presulfiding was done using the same procedure as for the HDM reaction. Using the HDM product oils prepared at 390 and at 410°C, the HDS reaction was performed under the following conditions: 370-410°C, 14 MPa, LHSV 0.5 h⁻¹, and H₂/oil ratio 840 Nm³/kl.

2.3. Preparation of Asphaltenes

Asphaltenes, which are *n*-heptane-insoluble and toluene-soluble materials, were prepared according to the following procedure. AL-AR and the bottom fraction (380°C+) of HDM or HDS product oils (10 g) were refluxed in *n*-heptane (300 ml) for 2 h, then cooled to room temperature. After the resulting mixture was filtrated, the residues were thoroughly washed with *n*-heptane and then Soxhlet-extracted with toluene. The extracts (asphaltenes) were dried at 110°C overnight. The asphaltene yields are listed in **Table 3**, where the yields of other fractions prepared by column separation⁽²⁷⁾ are also presented. One can see that the yield of saturate increases as hydrotreatings proceed, but the yields of aromatics, resins and asphaltenes decrease. Sludge formation was recognized in the HDM oil obtained at 420°C and in the HDS oils obtained at HDS temperature of 410°C.

2.4. Analysis

LD-MS spectra were measured by using a Thermoquest Vision 2000 Spectrometer using angiotensin as a calibration standard under the measurement conditions described elsewhere⁽¹⁸⁾. The average molecular weight (*MW*) and *MW* distribution of asphaltenes were then determined from these spectra. ¹H-NMR spectra of asphaltenes were recorded by using a Bruker MSL400. Asphaltene aromaticity was determined by using ¹³C-NMR; liquid state measurements (in CDCl₃) were carried out for 50,000 scans in a gated proton

Table 1 Properties of AL-AR

Density	[g/cm ³ @ 15°C]	0.9621
CCR	[wt%]	9.3
Sulfur	[wt%]	3.42
Nitrogen	[wtppm]	2100
Ni	[wtppm]	10
V	[wtppm]	35
Asphaltenes	[wt%]	3.0

Table 2 Catalyst Properties

Catalyst	Support	Metal loading [wt%]			SA ^{a)} [m ² /g]	PV ^{b)} [ml/g]	APD ^{c)} [nm]
		MoO ₃	NiO	CoO			
HDM	alumina	4.2	—	—	200	0.85	17
HDS	alumina	10.5	0.7	1.2	211	0.64	12

a) Surface area. b) Pore volume. c) Average pore diameter.

Table 3 Fraction Yields for Bottoms (380°C+) of AL-AR, HDM Oils and HDS Oils

	AL-AR	HDM oils			HDS oils			
HDM temperature [°C]	—	390	410	420	390	390	410	410
HDS temperature [°C]	—	—	—	—	370	410	370	410
Fraction yields [wt%]								
Saturate	48.2	59.2	61.6	64.3	67.4	72.8	71.9	74.7
Aromatics	37.1	31.0	30.1	28.3	26.1	22.2	23.6	21.1
Resins	11.3	8.9	7.5	6.5	6.1	4.5	4.4	4.0
Asphaltenes	3.4	0.9	0.8	0.5	0.4	0.4	0.1	0.1
Sludge	—	—	—	0.1	—	0.1	—	0.1

Fig. 1 Correction of Heteroatoms into Hydrocarbons

decoupled mode, where 0.02 M of $\text{Cr}(\text{acac})_3$ was added to obtain quantitative spectra. Elemental analyses were done by using a Yanako MT-5 with a combustion method.

2.5. Determination of Structural Parameters and Average Molecular Structure

Structural parameters (see **Nomenclatures**) and average molecular structure of asphaltenes were modeled by using a computer program developed by Sato²⁹⁾, which based on SAAH system developed by Katayama *et al.*^{30),31)}. In our method, we made the same assumptions about the modeling of the average molecular structure as those in the SAAH method; for example, (i) carbon-carbon double bond does not exist except for aromatic rings, (ii) each polycondensed aromatic core is connected with an alkyl chain, and (iii) naphthenic rings exist only on one side of the aromatic core. To obtain a hypothetical molecular structure, we corrected the heteroatoms such as sulfur and nitrogen as shown in Fig. 1.

Value in parentheses indicates number average molecular weight.

Fig. 2 LD-MS Spectra of Original and HDM Asphaltenes

3. Results and Discussion

3.1. Structural Change of Asphaltenes by HDM

Figure 2 shows LD-MS spectra of asphaltenes before and after the HDM reaction. The original asphaltenes showed a broad spectrum tailing to 5000 m/z . When the HDM temperature was increased, the spectra shifted towards lower mass and a new peak appeared in the range from 750 to 800 m/z for the asphaltenes obtained at above 400°C. A similar variation of MW distribution was previously observed for Kuwait-AR²⁷⁾. The MW of asphaltenes decreased with increasing HDM temperature.

Figure 3 shows aromaticity (fa) and aromatic ring number (Ra) as a function of HDM temperature. The fa monotonically increased from 0.59 to 0.75 with

Fig. 3 Variations of Aromaticity (f_a) and Aromatic Ring Number (R_a) with HDM Temperature

increasing HDM temperature, whereas R_a decreased from 25 to 17. No naphthenic rings were recognized in any asphaltenes after the HDM reaction. These findings suggest that hydrogenated asphaltenes converted to other fractions, and thus remained as asphaltenes without naphthenic rings. **Figure 4** shows the number of alkyl side chains (N) and the average length of these chains (L) as a function of HDM temperature. Whereas N gradually decreased with increasing HDM temperature, L remained constant up to 390°C and then rapidly decreased. These results agree with those by Koinuma *et al.*²⁶⁾, namely, the loss of alkyl side chains was a main reaction of asphaltenes in HDM hydrotreating. Based on our result, we conclude that the increase in f_a with increasing HDM temperature is due to the decrease in alkyl side chains.

Asphaltenes are well known to be adsorbed onto hydrotreating catalysts^{32),33)}, where the polarity of aromatic ring systems is significant. Therefore, it is interesting to examine the change in the shape of aromatic cores due to HDM reaction. Condensation index (CI) provides information on the shape of polycondensed aromatic cores³⁴⁾. **Figure 5** shows the change in CI as a function of HDM temperature. In our previous study²⁷⁾, the shape of aromatic cores for KW asphaltenes shifted towards peri-type due to the HDM reaction up to 410°C, whereas in this study the

Fig. 4 Variations of the Number (N) and Average Length (L) of Alkyl Side Chains with HDM Temperature

Fig. 5 Variation of Condensation Index (CI) with HDM Temperature

shape of AL asphaltenes remained unchanged. This suggests that, compared to KW asphaltenes, AL asphaltenes consist of similar aromatic cores in shape. A small decrease in CI at 420°C, which indicates a shift to cata-type, could be caused by sludge formation; this same shift to cata-type was seen for KW asphaltenes at the highest HDM temperature (430°C), where sludge formation occurred.

3. 2. Structural Change of Asphaltenes by HDS

Figure 6 shows the LD-MS spectra of asphaltenes

(A) HDM 390°C, (B) HDM 410°C. Value in parentheses indicates number average molecular weight.

Fig. 6 LD-MS Spectra of HDS Asphaltenes

after the HDS reaction. When the HDM temperature was 390°C, two peaks appeared, and then shifted to lower mass with increasing HDS temperature, resulting in a decrease in *MW* from *ca.* 1800 to 1500. When the HDM temperature was 410°C, although two peaks appeared, their shift to lower mass was slight, and thus the change in *MW* due to HDS reaction was slight. This indicates that further reactions of asphaltenes hydrotreated at higher temperature during the HDM reaction are not likely to proceed in the subsequent HDS reactions. The peaks appeared at the same mass (*ca.* 600 *m/z*) after the HDS reaction at 410°C, irrespective of HDM temperature. The molecule with *ca.* 600 *m/z* could be a minimum aromatic core of asphaltenes (details will be discussed in section 3.3.). Note that the *MWs* of asphaltenes after HDS at 370 and 390°C are higher than that before HDS when HDM temperature is 390°C. This unusual tendency was also observed for KW asphaltene¹⁸⁾ and could be explained by the selective reaction of asphaltenes with HDS catalysts: because asphaltenes with *MW* less than *ca.* 1500 are well-catalyzed by the HDS catalyst used, the *MW* of remaining asphaltenes after HDS reactions at 370 and

Fig. 7 Variations of Aromaticity (*fa*) and Aromatic Ring Number (*Ra*) with HDS Temperature

390°C becomes higher than that before the HDS if HDM temperature is 390°C.

Figure 7 shows *fa* and *Ra* after HDS reaction as a function of HDS temperature. For the HDM reactions at 390 and 410°C, *fa* increased with increasing HDS temperature. However, *fa* at the HDM temperature of 390°C did not exceed that at 410°C, irrespective of HDS temperature. The number of aromatic rings (*Ra*) roughly remained unchanged by the HDS reactions. In the HDS reaction, hydrogenation reaction of aromatic rings and/or cyclization of alkyl side chains was confirmed by the existence of naphthenic rings (Fig. 8). The number of naphthenic rings (*Rn*) decreased with increasing HDS temperature. The reason that the *Ra* remained unchanged even though some of the aromatic rings were hydrogenated to form naphthenic rings is unclear. However, one possible reason would be that strongly hydrogenated asphaltene convert to other fractions such as aromatics and resins, and weakly hydrogenated asphaltene with more aromatic rings remain as asphaltene. Another is that condensation reaction and/or dehydrogenation of naphthenic rings compensates for the hydrogenation-induced decrease in *Ra*. Evidence that supports this latter reason is that *Rn* decreased as HDS temperature increased.

Figure 9 shows the number (*N*) and average length (*L*) of alkyl side chains as a function of HDS tempera-

Fig. 8 Variation of Naphthenic Ring Number with HDS Temperature

Fig. 10 Variation of Condensation Index (CI) with HDS Temperature

Fig. 9 Variations of the Number (N) and Average Length (L) of Alkyl Side Chains with HDS Temperature

ture. When the HDM temperature was 390°C, N and L decreased with increasing HDS temperature. In contrast, when the HDM temperature was at 410°C, L decreased whereas N remained relatively unchanged with increasing HDS temperature. These results on the change of R_n , N , and L show that the increase in fa by HDS reaction (in Fig. 7) is caused by the loss of naphthenic rings and alkyl side chains. The shape of aromatic cores remained relatively unchanged by the HDS reaction (Fig. 10), similar to the effect by the HDM reaction. Note that the CI values (*ca.* 0.5) of asphaltenes after the HDS reaction are the same as that of coronene.

Fig. 11 Hypothetical Molecular Structures of Original Asphaltenes and Hydrotreated Asphaltenes

3. 3. Average Structure of Asphaltene Molecules

Using the structural parameters obtained with SAAH method, we calculated the hypothetical average structures of asphaltenes after HDM and subsequent HDS reactions, as shown in Fig. 11. In the modeling of asphaltenes, the metal contents (Ni and V) in an asphaltene molecule were so small that we neglected them; *e.g.* for original asphaltenes, which have the highest metal contents (Ni/V = 130/350 ppm), a Ni atom and a V atom exist roughly every 200 and 70 asphaltene mol-

Table 4 Comparison of Observed and Calculated Elemental Analyses and Structural Parameters for Original Asphaltenes and HDM Asphaltenes

	Elemental analyses [wt%]					Hydrogen distribution [%]				MW
	C	H	N	S	O	H _a	H _α	H _β	H _γ	
Original										
Observed	83.4	7.3	0.8	7.2	1.4	11.3	17.2	52.9	18.6	1793
Calculated	83.1	7.2	0.8	7.1	1.8	11.6	17.8	51.9	18.6	1804
HDM 390°C										
Observed	86.2	7.4	0.7	3.9	1.8	13.5	16.9	52.0	17.6	1626
Calculated	85.9	7.3	0.9	3.9	2.0	12.6	16.8	52.9	17.6	1634
HDM 410°C										
Observed	88.3	6.5	0.6	1.8	2.8	20.6	20.0	44.4	15.0	1190
Calculated	87.0	6.5	1.2	2.7	2.7	20.8	20.8	42.9	15.6	1200
HDM/HDS 390/410°C										
Observed	88.8	6.4	0.7	1.4	2.7	20.7	19.1	45.5	14.7	1522
Calculated	88.4	6.4	0.9	2.1	2.1	20.6	21.6	42.3	15.5	1520
HDM/HDS 410/410°C										
Observed	89.8	5.8	0.5	0.3	3.6	30.2	23.0	38.6	8.2	906
Calculated	89.0	5.9	1.5	0.0	3.5	32.1	28.3	34.0	5.7	903

ecules, respectively. For all asphaltenes, the elemental analysis, the hydrogen distribution, and the *MW* for the model structure agree well with the measured results; **Table 4** shows the comparison for representative samples of original asphaltenes and HDM asphaltenes (*i.e.*, asphaltenes after HDM reaction).

Asphaltenes after HDM reaction contain two aromatic cores that consist of 8-12 benzene rings. Compared to the original asphaltenes, HDM asphaltenes showed such structural features as: (i) smaller aromatic cores, (ii) fewer alkyl side chains, and (iii) less sulfur. In particular, the size of an aromatic core is significantly decreased at HDM temperatures above 400°C. Furthermore, nitrogen and oxygen functional groups still exist after the HDM reaction. These polar functional groups might act as the driving force of adsorption onto catalysts, and thus cause the deactivation. The reasons for the absence of naphthenic rings in HDM asphaltenes are probably that the HDM catalysts do not contain promoters (Ni or Co) which enhance hydrogenation of aromatic rings^{35),36)} and that the Mo content of the HDM catalysts is much lower than that of the HDS catalysts.

One can expect that average structure of HDS asphaltenes depends on HDM temperature as well as on HDS temperature. Based on our model, when the HDM temperature is 390°C, each molecule of HDS asphaltene contains three aromatic cores. This increase in the number of aromatic cores by HDS reaction results from a decrease of asphaltenes with a low *MW*. Namely, when the HDM temperature was 390°C, an asphaltene molecule with a high *MW* might not easily enter the HDS catalyst pore, and as a result, catalytic hydrogenation is insufficient for such asphaltenes. In fact, in our experiments, at that temperature, large amounts of asphaltenes with a high *MW*

still remain (**Fig. 6**). The presence of naphthenic rings in HDS asphaltenes could be explained by the high hydrogenation ability of the HDS catalysts which contain Ni and Co. When the HDM temperature was 410°C, asphaltenes had fewer alkyl side chains and aromatic cores similar to the asphaltenes obtained when the HDM temperature was 390°C.

An estimate of the *MW* of an aromatic core can be obtained by dividing the average *MW* asphaltenes by the condensation degree (*M*). For HDS asphaltenes, this calculated *MW* ranges from 450 to 620, which is consistent with values of the peak in **Fig. 6**. Therefore, the sharp peak appearing at lower mass can be assigned to an asphaltene molecule that has one aromatic core. In addition, coronene-type aromatics are the most stable aromatic cores of AL asphaltenes after hydrotreating.

4. Conclusions

Arabian light asphaltenes obtained after HDM reaction and subsequent HDS reactions were characterized by using elemental analyses, NMR, and LD-MS measurements. The results showed that an increase in HDM temperature caused a decrease in the number of aromatic rings and an increase in aromaticity, but no formation of naphthenic rings. They also showed that the loss of alkyl side chains was significant in HDM reactions. On the other hand, naphthenic rings were formed by HDS reaction, and their number decreased with increasing HDS temperature, resulting in an increase in aromaticity.

Using the structural parameters obtained with SAAH method, we calculated the hypothetical average structures of asphaltenes after HDM and HDS reactions. The results showed that the aromatic unit structure of

AL asphaltenes became coronene-type due to hydro-treating.

Acknowledgments

This work was performed as a research project of Petroleum Energy Center with a subsidy from the Ministry of International Trade and Industry, Japan.

Nomenclatures

<i>MW</i>	: number average molecular weight
<i>C_{ar}</i>	: total aromatic carbons
<i>C_{al}</i>	: total aliphatic carbons
<i>C_{ai}</i>	: internal aromatic carbons
<i>fa</i>	: aromaticity ($fa = C_{ar}/(C_{ar} + C_{al})$)
<i>H_a</i>	: proportion of aromatic hydrogen
<i>H_α</i>	: proportion of hydrogen α to aromatic ring
<i>H_β</i>	: proportion of hydrogen β to aromatic ring
<i>H_γ</i>	: proportion of hydrogen γ to aromatic ring
<i>R_a</i>	: aromatic ring number
<i>R_n</i>	: naphthenic ring number
<i>N</i>	: number of alkyl side chains
<i>L</i>	: average length of alkyl side chains
<i>M</i>	: number of fused ring units
<i>CI</i>	: condensation index ($CI = C_{ai}/(C_{ar} + C_{al})$)

References

- 1) Yen, T., Erdman, J., Pollack, S., *Anal. Chem.*, **33**, 1587 (1962).
- 2) Dickie, J., Yen, T., *Anal. Chem.*, **39**, 1847 (1967).
- 3) Ali, L., Ghannam, K., Rawi, J., *Fuel*, **69**, 519 (1990).
- 4) Speight, J., Moschopedis, S., *Prepr. ACS Div. Petrol. Chem.*, **24**, 910 (1979).
- 5) Straus, O., Mojelsky, T., Lown, E., *Fuel*, **71**, 1355 (1992).
- 6) Nakamura, M., Shiroto, Y., Takahashi, H., *Nippon Kagaku Kaishi*, **6**, 1037 (1980).
- 7) Shiroto, Y., Nakata, S., Fukui, Y., Takeuchi, C., *Ind. Eng. Chem., Process. Des. Dev.*, **22**, 248 (1983).
- 8) Miller, J., Fisher, R., Thiagarajan, R., Winans, R., Hunt, J., *Energy Fuels*, **12**, 1290 (1998).
- 9) Calemme, V., Iwanski, P., Nali, M., Scotti, R., Montanari, L., *Energy Fuels*, **9**, 225 (1995).
- 10) El-Mohamed, S., Achard, M., Hardouin, F., Gasparoux, H., *Fuel*, **65**, 1501 (1986).
- 11) Groenzin, H., Mullins, O., *Prep. ACS Div. Fuel Chem.*, **44**, 728 (1999).
- 12) Artok, L., Su, Y., Hirose, Y., Hosokawa, M., Murata, S., Nomura, M., *Energy Fuels*, **13**, 278 (1999).
- 13) Moschopedis, S., Speight, J., *Fuel*, **55**, 187 (1976).
- 14) In "The Chemistry and Technology of Petroleum," ed. by Speight, J., Marcel Dekker Inc., New York (1991), Chapter 11.
- 15) Yang, M., Eser, S., *Prep. ACS Div. Fuel Chem.*, **44**, 768 (1999).
- 16) Domin, M., Herod, A., Kandiyoti, R., Larsen, J., Lazaro, M., Li, S., Rahimi, P., *Energy Fuels*, **13**, 552 (1999).
- 17) Lazaro, M., Herod, A., Cocksedge, M., Domin, M., Kandiyoti, R., *Fuel*, **76**, 1225 (1997).
- 18) Seki, H., Kumata, F., *Prep. ACS Div. Fuel Chem.*, **44**, 786 (1999).
- 19) Thakur, D., Thomas, M., *Appl. Catalysis*, **15**, 197 (1985).
- 20) Marafi, M., Stanislaus, A., *Prep. ACS Div. Petrol. Chem.*, **42**, 573 (1997).
- 21) Pazos, J., Gonzalez, J., Guillen, A., *Ind. Eng. Chem. Des. Dev.*, **22**, 653 (1983).
- 22) Seki, H., Kumata, F., *Stud. In Surf. Sci. Catal.*, **126**, 357 (1999).
- 23) Seki, H., Yoshimoto, M., *Fuel Process. Technol.*, **69**, 229 (2001).
- 24) Seki, H., Yoshimoto, M., *Sekiyu Gakkaishi*, **44**, (2), 102 (2001).
- 25) Seki, H., Kumata, F., Saito, T., Yoshimoto, M., *Sekiyu Gakkaishi*, **44**, (3), 147 (2001).
- 26) Koinuma, Y., Kushiyama, S., Kobayashi, S., Aizawa, R., Inoue, K., Shimizu, Y., *Sekiyu Gakkaishi*, **31**, (3), 250 (1988).
- 27) Seki, H., Kumata, F., *Energy Fuels*, **14**, 980 (2000).
- 28) Asaoka, S., Nakata, S., Shiroto, Y., Takeuchi, C., *Ind. Eng. Chem. Des. Dev.*, **22**, 242 (1983).
- 29) Sato, S., *Sekiyu Gakkaishi*, **40**, (1), 46 (1997).
- 30) Katayama, Y., Sanada, Y., Ouchi, K., *Sekiyu Gakkaishi*, **21**, (3), 175 (1978).
- 31) Katayama, Y., Hosoi, T., Takeya, G., *Nippon Kagaku Kaishi*, 127 (1975).
- 32) Absi-Halabi, M., Stanislaus, A., Trimm, D., *Appl. Catalysis*, **72**, 193 (1991).
- 33) Quann, R., Ware, R., Hung, C., Wei, J., *Adv. In Chem. Eng.*, **14**, 95 (1988).
- 34) Rongbao, L., Zengmin, S., Bailing, L., *Fuel*, **67**, 565 (1988).
- 35) Stanislaus, A., Cooper, B., *Catal. Rev. Sci. Eng.*, **36**, 75 (1994).
- 36) In "Hydrotreating Catalysis," eds. by Topsøe, H., Clausen, B., Massoth, F., Springer, Berlin (1996), Chap. 5, p.155-217.

要 旨

二段直接脱硫プロセスにおける脱硫触媒の劣化（第5報）脱メタル
および脱硫反応後のアスファルテンのキャラクタリゼーション関 浩幸^{†1)}, 佐藤 信也^{†2)}, 吉本 昌雄^{†1)}^{†1)} (財)石油産業活性化センター, 213-0012 川崎市高津区坂戸 3-2-1 KSP12F-1237^{†2)} 資源環境技術総合研究所, 305-5869 茨城県つくば市小野川 16-3

アラブライト常圧残油を用いて脱メタルおよび脱硫の二段反応を行い、各々で得られたアスファルテン平均構造の変化を調べた。脱メタル反応後には、芳香環数および脂肪族側鎖の減少に伴い、芳香族性の増加が見られた。一方、脱硫反応では主にナフテン環の生成が顕著であり、脱硫温度の増加とともに減少する傾向が見られた。そのため、脱硫温度とともに芳香族性が

増加した。片山らの SAAH 法によって得られた構造パラメーターを元に、各反応における平均構造を提案した。この構造変化からは、アラブライト系アスファルテンの芳香族単位骨格は脱硫反応の進行とともにコロネン構造に近づくことが推測される。

.....

Keywords

Hydrodemetallization, Hydrodesulfurization, Asphaltene, Aromatic ring, Naphthenic ring, LD-MS