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Behaviors of oil-soluble molybdenum complexes to form very fine MoS_2 particles in vacuum residue ☆

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Abstract

Dispersion and thermal behaviors of oil-soluble Mo-dithiocarbamate (Mo-DTC) and Mo-dithiophosphate (Mo-DTP) as the MoS_2 catalyst precursors were studied in petroleum vacuum residue (VR) using FT-Far IR, XRD and TEM. FT-Far IR was proved to detect the Mo complexes and their derived MoS_2 in VR without the interference of the complicated organic matrix. Their transformation into MoS_2 was identified by detecting the changes in the ligand bonds and crystal structure. These complexes were found to be distributed in asphaltene (or maltene) by fractionation with hexane due to their solubility in the heavy oil, ruling out any chemical interaction of the complex with asphaltene. Mo-DTC was found to be decomposed at 350 °C to form definite MoS_2 in VR. Mo-DTP started its decomposition around 200 °C, and however, no definite formation of MoS_2 was confirmed by heating up to 500 °C. Dispersion of the complexes in VR and asphalthene was always good as indicated by TEM. Both complexes in VR at 380 °C under hydrogenation (HYD) conditions provided more or less MoS_2. H_2S and reactive sulfur species were assumed to accelerate the transformation of the Mo complex to MoS_2 during HYD reaction. Some difficulty of Mo-DTP to be transformed quantitatively into definite MoS_2 in VR may explain its poor activity for up-grading VR. © 2002 Published by Elsevier Science Ltd.

Keywords: Mo complex; MoS_2; FT-Far IR; Vacuum residue

1. Introduction

Highly dispersed sulfide catalyst of fine particles has been reported very active for up-grading heavy petroleum and liquefaction of coal [1–6]. The best precursor complex is now looked for in order to reduce the cost by the highest performance. For this purpose, the behavior of the complex is wanted to be clarified when heated in the heavy feed under the reaction atmosphere. Some catalyst precursors were reported to have chemical interaction with VR fraction [1]. However, chemical identification and analysis in structural changes of the complex are not easy because the strong interference by the complicated organic matrix of the feed is inevitable.

The present study reports the usefulness of FT-Far IR, XRD and TEM to elucidate the structure of the precursor complex in the petroleum vacuum residue and its transformation into MoS_2. The FT-Far IR can identify the Mo ligand bonds in the complicated organic matrix. Mo-dithiocarbamate (Mo-DTC) and Mo-dithiophosphate (Mo-DTP) (Fig. 1) have been reported to show the different activity for the up-grading of VR [7]. Analyses in their structural changes when heated in VR are expected to suggest the reason why their activities are different.

2. Experimental

2.1. Materials

Mo-DTC and Mo-DTP (their structures are shown in Fig. 1) used as the precursors of the catalyst were commercially available in forms of crystal and solution, respectively. Commercially available MoS_2 powder was used as a reference. Arabian heavy vacuum residue was used in this study. Their properties are summarized in Table 1. Its maltene and asphaltene were separated by *n*-hexane extraction.

The Mo complex was mixed with VR or asphaltene. A small amount of toluene was added to disperse well the complex in asphaltene under an ultrasonic irradiation.

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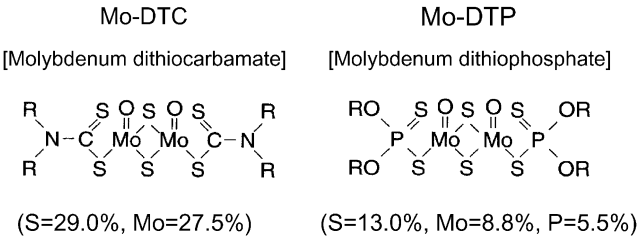

Fig. 1. Mo complexes for catalyst precursor.

2.2. Heat treatment

The mixture of Mo complex with VR was heated at 110 °C for 1 h for well dispersion, and then hydrotreated at 380 °C over the decomposition temperature of complexes in a mini-autoclave under 10 MPa H_2. The heated mixture was extracted with hexane to separate the maltene and asphaltene fractions. Either maltene or asphaltene fraction might carry the Mo complex or its decomposed derivative.

2.3. Analysis

The thermal behavior of the Mo complexes was studied, using TGA (Seiko, SSC/5200) by their weight changes. The complex and its decomposed products in the residue were analyzed with FT-Far IR (JASCO-620) and X-ray diffractometer with vertical goniometer (Rigaku, Geigerflex) for solid sample and with horizontal goniometer (Rigaku, RINT Ultima$^+$) for liquid sample. The complex in VR was observed under TEM (JEOL, JEX-100CX).

3. Results

3.1. Thermal stability of Mo-DTC and Mo-DTP

TG and DTA curves of Mo-DTC and Mo-DTP are shown in Fig. 2a and b, respectively. In the case of Mo-DTC (Fig. 2a), DTA shows three endothermic peaks at 180, 274 and 336 °C. These peaks suggest that thermal degradation of the ligand happens stepwise. Two peaks of DTA were observed below 274 °C without any significant weight loss, suggesting some structure changes without degradation. Real decomposition of the complex occurred at 336 °C. The yield of residue after the decomposition was 48 wt%. The theoretical yield of MoS_2 from the complex is calculated as 47 wt%. The formation of MoS_2 through the thermal degradation of the complex is strongly suggested. Mo-DTP in solution showed two regions of weight loss (Fig. 2b). The first one was rapid, providing a sharp DTA peak, owing to

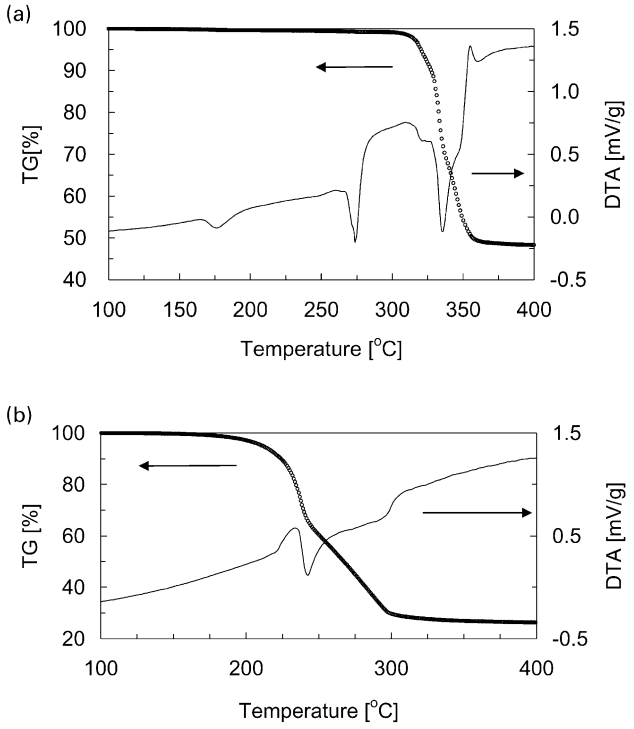

Fig. 2. (a) TG and DTA curves of Mo-DTC (heating rate; 10 °C/min); (b) TG and DTA curves of Mo-DTP (heating rate; 10 °C/min).

solvent vaporization. The real decomposition of the complex occurred slowly above 244 °C, providing slow weight loss and endotherm up to 300 °C. The yield of residue after the decomposition was around 26 wt%. The yield was larger than the theoretical yield of MoS_2 from the complex. According to the results, some of the ligand elements such as O or P are being suspected to remain around MoS_x. It is suggested that MoS_2 is not to be formed from Mo-DTP through the thermal decomposition (under N_2 flow).

Fig. 3 shows FT-Far IR spectra of Mo-DTC, Mo-DTP and their derivatives treated under nitrogen at temperatures up to 400 °C. Mo-DTC showed peaks at 478, 381 and 339 cm^{-1} as shown in Fig. 3A. The same spectra were observed after the heat treatment at temperatures up to 260 °C. The heat treatment at 300 °C converted the complex to MoS_2 that showed a sharp peak at 384 cm^{-1}. Fig. 3C shows FT-Far IR spectrum of commercial MoS_2. A distinct and sharp peak was observed at 380 cm^{-1} which appeared characteristic to MoS_2, being different from Mo–S bond at 478 cm^{-1} in the complex. The heat treatment at 400 °C provided a peak at the same position.

Mo-DTP showed peaks at 475, 356, 328 cm^{-1} as shown in Fig. 3B. The treatment at 350 °C decomposed the

Table 1
Elemental analysis of AHVR

C (wt%)	H (wt%)	N (wt%)	Others (wt%)	H/C	N/C	Ni + V (ppm)
84.0	9.9	0.5	5.7	1.40	0.005	210

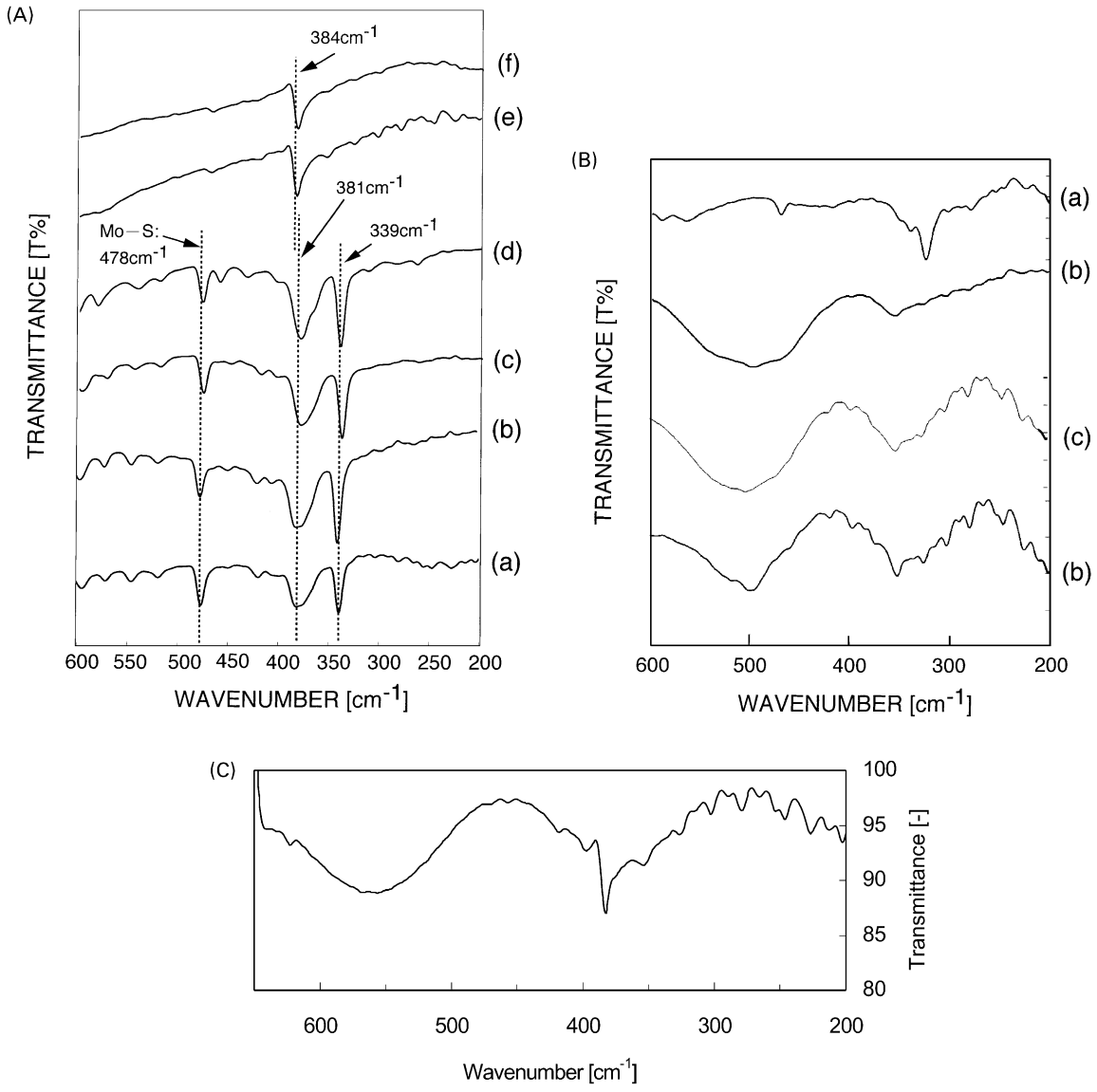

Fig. 3. FT-Far IR spectra of Mo-DTC; (A) raw: (a) and heat treated at (b): 200 °C, (c): 250 °C, (d): 260 °C, (e): 300 °C, (f): 400 °C. (B) FT-Far IR spectra of Mo-DTP; raw: (a) and heat treated at; (b): 350 °C, (c): 400 °C, (d): 500 °C FT-Far IR spectra of MoS_2. (C) FT-Far IR spectrum of MoS_2.

complex, providing very broad peaks around 450–550 cm^{-1}, however, no definite peak ascribed to MoS_2 was observed. The broad peaks around 250–400 cm^{-1} observed in the spectra after the heat treatment above 350 °C could be assigned to amorphous MoS [8], of which Mo/S atomic ratio (1:1) was found in the present study by XPS. In addition, the heat-treated sample was found to carry some P by XPS.

XRD of Mo-DTC showed its decomposition by 300 °C as shown in Fig. 4. Broad diffraction peaks at 14.3, 32.7 and 58.3° suggest the formation of MoS_2 with very low crystalinity. Mo-DTP dissolved in the oil did not show any diffraction pattern by XRD. Heating at 220 °C removed the oil, leaving solid, which showed no significant diffraction peak to indicate the formation of MoS_2. The solid particles obtained from Mo-DTP after heating up to 500 °C showed no distinct diffraction peaks ascribed to MoS_2. Mo-DTP showed a distinct P (v) peak in ^{31}P NMR, however, no P peak was found after the heat treatment at 400 °C.

3.2. Distribution of Mo-DTC and Mo-DTP in VR and asphalthenes

Fig. 5 shows FT-Far IR spectra of Mo-DTC and Mo-DTP dispersed in VR, distributed in HS and HI fractions after the fractionation by hexane, respectively. Mo-DTC and Mo-DTP in VR showed definite peaks as observed with their original forms. The former complex was found exclusively in the HI fraction as shown in Fig. 5a, while hexane soluble

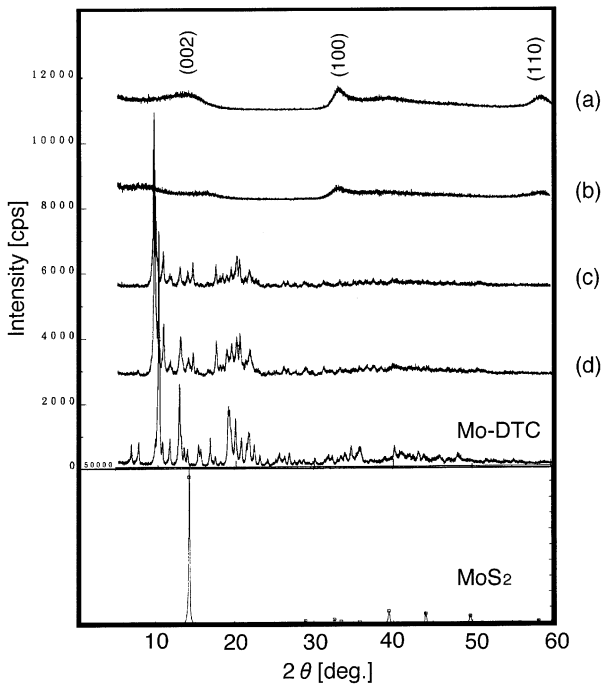

Fig. 4. XRD patterns of Mo-DTC heat-treated at; (a): 300 °C, (b): 270 °C, (c): 250 °C, (d): 200 °C.

Mo-DTP was found exclusively in the HS fraction as shown in Fig. 5b. No changes were found in both spectra of Mo-DTC in HI and Mo-DTP in HS, comparing with the spectra of their original complexes in VR. Solubility of the complexes in *n*-hexane appears to determine their distribution in the fractions. So far no particular chemical interaction is suggested between the Mo complex and HS or HI fraction of VR.

Fig. 6 shows FT-Far IR spectra of Mo-DTC and Mo-DTP dispersed in asphalthenes after mixing with toluene at 120 °C, followed by drying at 80 °C in vacuum for 2 h. Both Mo complexes showed their original characteristic spectra being dispersed in the asphalthenes. No chemical interaction is suggested.

Fig. 7 shows TEM photographs of Mo-DTP and Mo-DTC in the asphalthene. Both complexes were found highly dispersed in particles of asphalthene at room temperature, showing some stacking.

3.3. Heat treatment of Mo-DTC and Mo-DTP in asphalthene

Fig. 8 shows FT-Far IR spectra of Mo-DTC and Mo-DTP in asphalthene after the heat treatment at 370 °C. Mo-DTC certainly provided MoS_2 as indicated by the peak at 386 cm^{-1} shown in Fig. 8a. In contrast, Mo-DTP did not give any definite peak ascribed to MoS_2 by the heat treatment at 380 °C in the asphalthene as shown in Fig. 8b. No distinct peak ascribed to either the complex or MoS_2 was observed.

3.4. Mo-DTC and Mo-DTP in VR after the hydrotreatment reaction

Fig. 9a and b show FT-Far IR spectra of Mo-DTC and Mo-DTP in VR after the hydrotreatment at 380 °C, respectively. The HI in the hydrotreated VR carried MoS_2 as

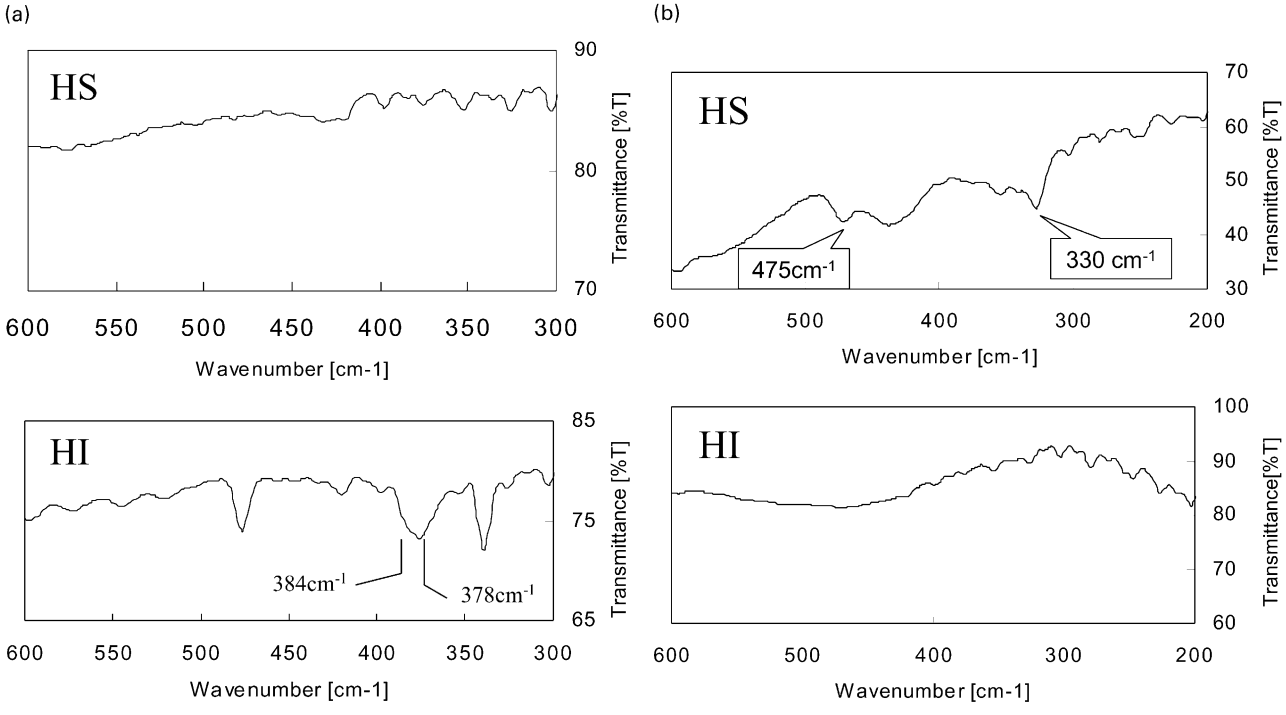

Fig. 5. (a) Distribution of Mo-DTC in VR; (b) Distribution of Mo-DTP in VR.

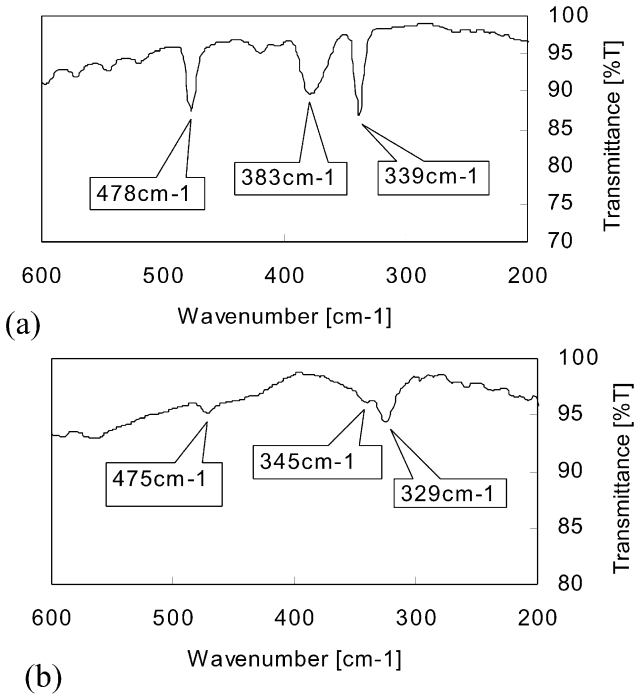

Fig. 6. FT-Far IR spectra of Mo complexes dispersed in asphaltene: (a) Mo-DTC, (b) Mo-DTP.

shown by peak at 386 cm^{-1} in both spectra. Neither Mo complex nor its sulfide was found in the HS fraction. The XRD profiles of HI after the hydrotreatment are shown in Fig. 10. Mo-DTC (Fig. 10a) provided three broad diffraction peaks at 33° (100), 39° (103) and 59° (110). MoS_2 of poor crystal was definitely produced. Although Mo-DTP (Fig. 10b) also provided three diffraction peaks under hydro treatment condition, the peaks were much broader and weaker than those of Mo-DTC.

4. Discussions

The present study proved that FT-Far IR, XRD and TEM were excellent tools to follow the thermal stability, dispersion and transformation into Mo sulfide of Mo-DTC and

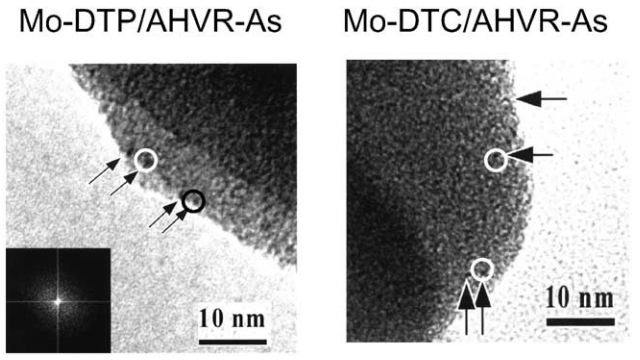

Fig. 7. TEM photographs of catalyst precursor in asphaltene.

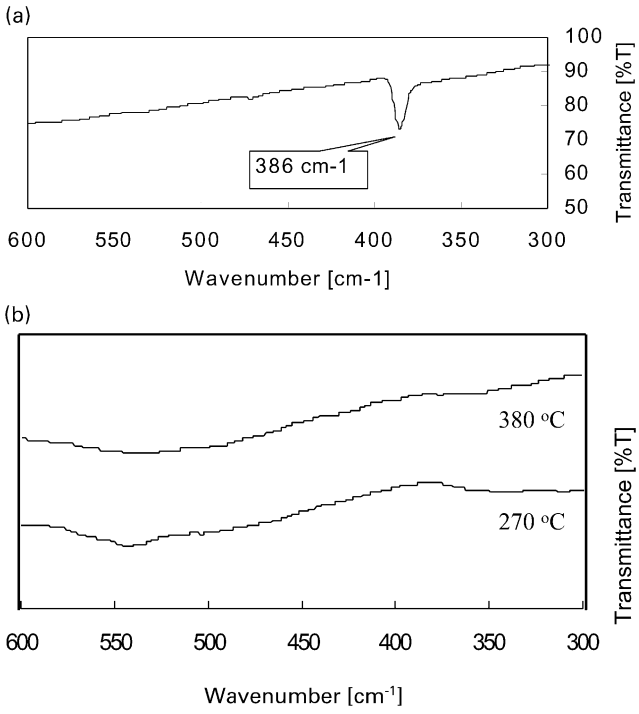

Fig. 8. (a) FT-Far IR spectrum of Mo-DTC in asphaltene after heat treatment at 370 °C; (b) FT-Far IR spectra of Mo-DTP in asphaltene after heat treatment.

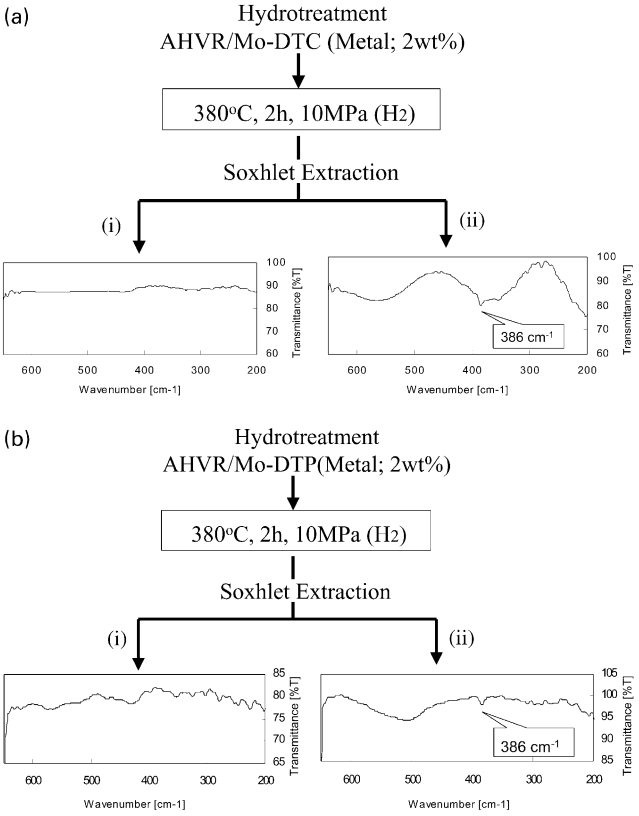

Fig. 9. (a) FT-Far IR spectra of Mo-DTC in VR after hydrotreatment (i) soluble, (ii) insoluble fraction; (b) FT-Far IR spectra of Mo-DTP in VR after hydrotreatment (i) soluble, (ii) insoluble fraction.

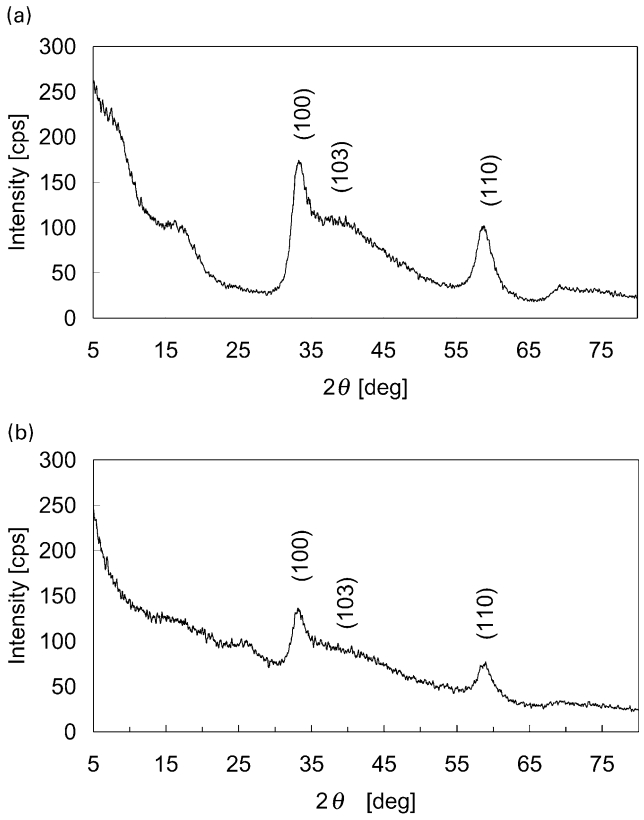

Fig. 10. XRD pattern of HI fraction of AHVR/Mo-DTC (Mo/VR = 2%) after hydrotreatment reaction; 380 °C, 2 h, 10 MPa:H_2 (b) XRD pattern of HI fraction of AHVR/Mo-DTP (Mo/VR = 2%) after hydrotreatment reaction; 380 °C, 2 h, 10 MPa:H_2.

Mo-DTP in VR, or in asphalthene or maltene after the fractionation. FT-Far IR is not at all interfered to detect Mo–S bond by the complicated organic matrix.

Thus, it was found that Mo-DTC provides MoS_2 when heated with and without VR or asphalthene. MoS_2 was formed after the heat treatment at 270 °C confirmed by XRD. DTA peak at 274 °C may indicate the formation of MoS_2 structure surrounded by other parts of the ligand that still stays near the MoS_2. In contrast, Mo-DTP lost its complex structure by heating at 300 °C, however, amorphous MoS with some amount of P appeared to be produced instead of definite MoS_2.

Under hydrotreatment conditions, Mo-DTC provided definitely MoS_2. In contrast, Mo-DTP gave MoS_2 of lower crystallinity solid particles as shown by XRD and FT-Far IR. Sulfiding may not be completed even under the hydrotreatment conditions. Strong coordination of P to Mo may inhibit the formation of MoS_2 from Mo-DTP even in VR or asphalthene under the significant presence of H_2S, although P was not found by ^{31}P NMR after the heat treatment.

The Mo complexes dispersed in VR are extracted according to their solubility, distributing in HS (Mo-DTP) or HI (Mo-DTC), respectively, after the extraction by *n*-hexane. So far strong chemical interaction of the complex with any particular component in VR or asphalthenes is suggested. Simple physical dispersion is suggested when the Mo complexes were dispersed in asphalthene. Although rather high concentration of the complex may hide the interaction.

Both the complexes are well dispersed in asphalthenes as observed by TEM. Both the complexes provided solid fine particles with small stacking dispersed in asphalthenes at room temperature.

The present results suggest the following conclusions:

1. The difference reported [7] in catalytic activities of Mo-DTC and Mo-DTP can be ascribed to the different extent of MoS_2 formation from the complexes under hydrotreatment conditions. Stronger sulfiding of Mo-DTP is expected to increase its activity by completing the formation.
2. MoS_2 or solid Mo compounds derived from Mo-DTC and Mo-DTP are fine particles of very low crystallinity that can be highly dispersed in VR or asphalthenes.
3. There is no particular interaction of the complex with particular functions such as heteroatomic groups in VR or asphalthene. Nevertheless resultant MoS_2 or solid Mo compounds produced by heating or hydrotreating in VR are dispersed well in asphalthene. Such solid particles can be physically dispersed and allowed to stay in asphalthene while the asphalthene micelle is dissolved or dispersed in toluene or malthene while heating.
4. Thermal decomposition of Mo-DTP stoichiometrically gave MoS_2, whereas Mo-DTP appears to provide MoS in the presence of remaining phosphorous species. Remaining phosphorous species may retard conversion of MoS to MoS_2 in VR.

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