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Use of a Dispersed Molybdenum Catalyst and Mechanistic Studies for Upgrading Extra-Heavy Crude Oil Using Methane as Source of Hydrogen

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A dispersed molybdenum catalyst, derived from $\text{MoO}_2(\text{acac})_2$ (where acac = acetylacetonate), was used for upgrading extra-heavy crude oil in the presence of methane as source of hydrogen. The experiments were carried out in a batch reactor at a final CH_4 pressure of 11 MPa, 410 °C, for 1 h. An increase of 7° in the API gravity, 16% of reduction in sulfur content, and 55% conversion of the >500 °C fraction with respect to the original crude was found. The catalyst was analyzed by XPS and EDAX from the coke isolated from the upgrading reaction and it was confirmed that molybdenum is present as MoS_2 . By XPS and SIMS, mechanistic studies were carried out using MoS_2 synthesized on a pure molybdenum sheet. A mechanism for addition of the methane to crude oil is proposed which involves activation of CH_4 by the MoS_2 catalyst generating CH_x and H_{4-x} species on the catalyst surface (where $x = 1, 2$, or 3). The CH_x moiety can be added to the hydrocarbon molecules, forming methylated products. By carbon isotope ratio mass spectrometry analysis, labeled methane ($^{13}\text{CH}_4$) was found to incorporate into the crude oil (estimated value 0.01% w/w) giving conclusive evidence on the involvement of CH_4 in the heavy crude oil upgrading processes.

Introduction

The use of dispersed metal catalysts represents a feasible alternative for the upgrading of heavy oils and its fractions mainly due to the possibility of obtaining high dispersion of the active metal species with the concurrent high activity toward the desired reactions.¹ Generally, these catalytic systems are not recovered after the upgrading reaction and since the pioneering work by Aldridge and Bearden,² have been successfully applied to the liquefaction of coal,^{1–4} the hydroconversion of heavy oil residue,^{5,6} and heavy and extra-heavy crude oil upgrading.^{7–9}

A water- or oil-soluble metal catalyst precursor is normally introduced to the crude oil and it decomposes under thermal treatment and gives rise to a slurry of fine solid particles. The sulfided catalyst is subse-

quently produced by the in situ reaction of the precursor with sources of sulfur in the reaction mixture.^{1,2} Several metals have been studied and, in general, Mo, Ni, and Fe showed higher conversion and lower asphaltene contents than other metals evaluated (Cr, V, and Co).^{2,5,6} The concentration as well as the cost of the metals has been considered. In general, concentrations between 200 and 600 ppm are used and iron or molybdenum catalysts are the preferred metals.^{1–9}

The use of methane as hydrogen source represents a further improvement of the economical aspects of the extra-heavy crude oil^{10–13} and coal^{14–21} upgrading technologies mainly because a hydrogen generation plant is not necessary. Using this concept, the reaction of Hamaca crude oil (°API = 8.3) under thermal conditions (380 °C, 11.0 MPa of CH_4 for 4 h residence time) and in

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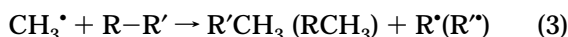
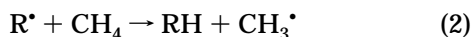
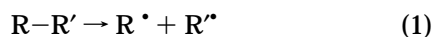
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the presence of water as additive led to a decrease of 2 orders of magnitude in the viscosity of the upgraded product (from 500 to 1.99 Pa s at 30 °C), conversion of the >540 °C fraction of 60%, and 11.3% reduction of sulfur with respect to the original crude.¹² A reaction carried out under nitrogen as an inert gas (control experiment) led to a product with higher viscosity (2.6 Pa s), lower conversion of the heavy fraction (54%), and less sulfur reduction (8.3%), indicating that methane is involved in the upgrading reactions and, most probably, was behaving as a source of hydrogen for the thermal processes.¹²

According to ¹H- and ²D-NMR, an increase in the amount of α-hydrogen bonded to aromatic rings was observed and was attributed to the incorporation of methyl groups to the molecules of the crude oil following a free-radical pathway outlined in eqs 1–3.¹²



where R and R' are hydrocarbons (naphthenic or aromatic).

In eq 1, free radicals (R[•]) are generated by thermal cracking of hydrocarbon molecules (R–R') due to the high temperatures and pressures used, followed by proton abstraction to produce methyl radical from methane (eq 2). The former species reacts (eq 3) with hydrocarbon molecules producing methylated species (RCH₃) and free radicals, R[•] to continue the chain process.¹²

In agreement with these results, Egiebor and Gray found methyl and dimethyl products by GC analysis of the donor solvent (tetralin) which was attributed to direct alkylation by reaction with methane in their iron catalyzed coal liquefaction experiments.¹⁶

Maier and co-workers studied the conversion of coal with methane in the presence of alkaline catalysts and various reactive gases under pyrolysis conditions (2 MPa and 700 °C).^{17,18} They found an increase of liquids products from coal pyrolysis in the presence of CH₄ which was attributed to the additional pyrolysis of methane and not to any cross reactions. However, a relative increase in the content of alkylated aromatics was observed when methane was used, which is consistent with the pathway shown in eqs 1–3.^{17–18}

Using an alumina supported molybdenum–nickel catalyst, Ovalles et al. obtained a relatively higher percentage of desulfurization (28%) and lower percentage of asphaltenes (9.3%) at a similar percentage of conversion of the >540 °C fraction than those found in thermal reaction (11% and 11.8%, respectively).^{11,13} These results indicate that methane can be catalytically activated and used for upgrading extra-heavy crude oil. The observed relative order of reactivity for the catalytic upgrading of Hamaca crude oil was found to be H₂ > CH₄ > N₂.

In the literature discussed, the lack of fundamental knowledge as well as catalyst characterization is evident.^{10–16} For this reason, we concentrated on studying a dispersed molybdenum catalyst, derived from

Table 1. Analysis of the Hamaca Crude Oil Used for the Upgrading Reactions

API gravity at 15.6 °C	8.7
water (% w/w)	<1
H/C wt ratio	0.115
sulfur (% w/w)	3.40
nickel (ppm)	91.9
vanadium (ppm)	412
asphaltenes (% w/w) ^a	12.5
% of residue (500+ °C)	57
viscosity at 30 °C (Pa s)	500

^a Percentage of asphaltenes precipitated with heptane using IP Method No. 143.

MoO₂(acac)₂ (where acac = acetylacetonate), for the upgrading of extra-heavy crude oil in order to understand the mechanism for methane activation using the latter as source of hydrogen. The molybdenum catalyst was analyzed by XPS and EDAX from the coke isolated from the upgrading reaction. Combining XPS and SIMS, mechanistic studies were carried out using a thin MoS₂ film synthesized on top of a pure molybdenum sheet (model system). Also, upgrading experiments were performed using ¹²CH₄, ¹³CH₄, and CD₄ and the products were analyzed by mass spectrometry. Finally, the most probable mechanism for methane activation was proposed and the amount of methane incorporation to the crude oil was estimated.

Experimental Section

All solvents were analytical grade and were used as received. Hydrogen, argon, and nitrogen gases were purchased from Gases Industriales de Venezuela. Methane was supplied by Matheson (99.99%). Methane-*d*₄ (99%) and ¹³CH₄ (99%) were purchased from Icon Stable Isotopes. MoO₂(acac)₂ was purchased from Aldrich and was used as received.

Sulfur analyses were carried out by X-ray fluorescence in a Phillips instrument, model PW-1400. Viscosities of the crude oils were measured in a Brookfield apparatus, model RVTDV-II. Nuclear magnetic resonance spectra were recorded in a Bruker spectrometer, model ACP 400.

The crude oil employed in this work came from the Hamaca oil field in the Orinoco Belt and its analysis can be found in Table 1. The percentages of volatile material were determined by the method reported by Ceballo and co-workers using a Hewlett-Packard gas chromatograph, model 5880.²²

The percentage of conversion of the residue >500 °C was defined as

$$\left\{ \frac{(\% \text{ of residue } > 500 \text{ }^{\circ}\text{C in crude oil}) - (\% \text{ of residue } > 500 \text{ }^{\circ}\text{C in upgraded product})}{(\% \text{ of residue } > 500 \text{ }^{\circ}\text{C in crude oil})} \right\} \times 100$$

Upgrading reactions were carried out in a stainless steel 300 mL batch Parr reactor equipped with a magnetic stirrer, a heating mantle, and a temperature controller, model 4561. In a typical experiment, the reactor was loaded with 40 g of Hamaca crude oil, containing 250 ppm of Mo metal as MoO₂-(acac)₂, and pressurized to 4.8 MPa for methane and argon and 5.5 MPa for hydrogen. The reactor was heated at 5 °C/min to 410 °C generating a final pressure of approximately 11 MPa for 1 h. The reactor was then cooled to room temperature, and the treated crude oil sample was separated and submitted for analysis. Gas production was lower than 10% for all the experiments reported and the results are the average of at least two different reactions.

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X-ray photoelectron spectroscopic (XPS) and secondary ion mass spectrometry (SIMS) experiments were carried out in using a Leybold-Heraeus surface analysis system which was operated with an aluminum anode (1486.6 eV). Pass energy was set at a constant value of 50 eV and the data acquisition and manipulation were performed using a 486 IBM compatible computer. The instrument sensitivity factors used for scaling the photoelectron peak areas were calculated using the method reported by Leon and Carrazza.²³

MoS₂ supported on molybdenum metal was synthesized using a continuous flow glass reactor. A pure molybdenum sheet was oxidized with air at 350 °C for 1 h, reduced with hydrogen at 350 °C for 2 h, and sulfided with 2–5% v/v of H₂S in H₂ at 380 °C for 1 h. Methane-containing reaction was carried out at 0.3 MPa, 420 °C, for 2 h. The MoS₂/Mo sheet was transferred to the surface analysis system using a nitrogen-filled drybox. The SIMS and etching experiments were carried out with an argon ion gun operated with an accelerating voltage of 3 keV and at an emission current density at the sample of approximately 0.3 μA/cm² as estimated using depth profiling data.

A stainless steel 10 mL batch reactor was used for the reactions carried out with ¹³CH₄ and CD₄. The design of this reactor was reported elsewhere.²⁴ Due to the narrow inlet of the reactor, the crude oil (5 mL), containing 250 ppm of Mo metal as MoO₂(acac)₂, was warmed and introduced by means of a syringe. A heating tape and a glass wool cover were used to heat the reactor. The final pressures and the residence times used were the same reported above. For comparison purposes, experiments with CH₄ with and without catalyst were carried out using the same apparatus. The gases in the reactor were injected directly to the mass spectrometer (Micromass model ZAB-SEQ operated at 70 eV) and the peaks in the 29–39 *m/z* range were recorded.

Carbon isotopic analysis was carried out using a method similar to static combustion technique described by Sofer.²⁵ Portions of crude oil and samples of reference material (NBS-22) were prepared for carbon isotopic analyses using the method reported in the literature.²⁶ In a typical preparation, 1 g of fired wire copper oxide in a Pyrex tube (~1 cm of packing in the 22 cm × 8 mm, i.d. tube) followed by ~1 mg of sample, using borosilicate capillary tube (via capillary rise); the portion of the capillary tube which contains approximately the necessary weight of sample is broken off and dropped into the combustion tube.

The tubes were prepared for combustion by evacuating on a vacuum line (0.1 KPa) and sealing with a torch at a point ~18–19 cm up from closed end. An ultra-tore union was used to connect the tubes to the vacuum line. The evacuated and seal tubes were placed horizontally on a stainless steel rack to guarantee good distribution of the copper oxide in the tube. The loaded rack was placed in an electric furnace, and the temperature was stabilized at 550 °C for 8 h.

After combustion, the rack is left to cool overnight. Following combustion, the tubes were connected to a vacuum line (10 Pa), opened with a tube cracker (as described by DesMarais et al.²⁷) for extraction of pure CO₂ by cryogenical distillation. Water was removed using a ethanol/dry ice trap (ca –80 °C). Afterwards, the CO₂ was collected in a liquid nitrogen cooled ampule which was sealed with gas-tight valves and transferred directly to the inlet system of an isotope ratio mass spectrometer (Finnigan MAT) for carbon isotopic analyses. The ¹³C/¹²C isotopic ratios and the δ¹³C (‰) values were reported

Table 2. Upgrading of Extra-Heavy Crude Oil Using MoO₂(acac)₂ as Organometallic Precursor^a

run	gas used	°API ^b	HDS ^c (wt %)	% conv. >500 °C ^d	coke (wt %)	gases (wt %)	liquids (wt %)
Hamaca crude oil		8.7	(3.40% S)				
control ^e	CH ₄	14.6	10.0	41	7.7	4.6	87.7
1	CH ₄	15.9	15.6	55	6.3	4.6	89.1
2	argon	12.7	8.0	43	12.1	3.4	84.5
3	H ₂	15.1	22.3	65	6.5	3.0	90.5

^a The reactions were carried out in a 300 mL batch reactor at 410 °C, 250 ppm of metal, 11 MPa of final pressure for a 1 h period. The results are the average of at least two different reactions. Where acac = acetylacetonate. ^b API gravity of the upgraded crude oil. ^c Percentage of desulfurization with respect to the starting crude oil. ^d Percentage of conversion of the residue >500 °C as defined in the experimental part. ^e Control experiment, i.e., no catalyst was used.

relative to the PDB standard (¹³C/¹²C = 0.011 237) and isobaric interferences were corrected. The formula used for δ¹³C is the following:^{26a}

$$\delta^{13}\text{C} = [({}^{13}\text{C}/{}^{12}\text{C})_{\text{sample}}/({}^{13}\text{C}/{}^{12}\text{C})_{\text{standard}}] - 1 \times 1000$$

It is important to point out that the normal experimental error for this technique is reported to be ±0.05‰.²⁷

Results and Discussion

Upgrading Reactions and Catalyst Characterization. The reaction of Hamaca extra-heavy crude oil (Table 1) at 11 MPa of methane and 410 °C for 1 h (Table 2, control run) led to an increase of 6° in the API gravity of the upgraded product, 10% of reduction in sulfur content and 41% conversion of the >500 °C fraction with respect to the original crude. An analogous reaction carried out in the presence of MoO₂(acac)₂ as dispersed catalyst (Table 2, run 1) yielded a product with slightly higher API gravity (16°), higher reduction in sulfur content (16%) and higher conversion of the heavy fraction (55%). Additionally, in the presence of the catalyst, a reduction of coke formation (from 7.7 to 6.3%) was observed in comparison with the control experiment. These results strongly indicate that the presence of the molybdenum catalyst is necessary in order to enhance the upgrading of extra-heavy crude oil in the presence of methane.

A reaction carried out in an inert argon atmosphere (Table 2, run 2) yielded a product with lower API gravity (8°), less reduction of sulfur content (8%), and lower conversion of the >500 °C fraction with respect to the methane-containing experiment (Table 2, run 1). These results indicate that methane is involved, as a source of hydrogen, in the upgrading reaction and that it can be activated by the metal catalyst. In order to understand the later reaction, mechanistic studies were carried out and the results are presented in the next section.

Evidence of the role of methane in the catalytic upgrading process can be found in Figure 1. At 410 °C for 1 h, the percentage of conversion of the fraction >500 °C increase from 28 to 55%, the desulfurization from 10 to 16% and the coke formation decrease from 9 to 6% as the methane final pressure increases from 2.7 to 11 MPa in the presence of MoO₂(acac)₂ as dispersed catalyst.

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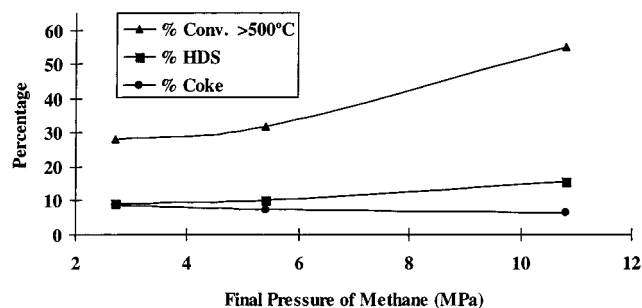


Figure 1. Effects of methane final pressure on the percentage of conversion of >500 °C fraction, percentage of desulfurization, and coke formation of upgraded products. Same conditions as Table 2.

Table 3. Results of the XPS Analysis of the Coke Isolated from Upgraded Hamaca Crude Oil Using MoO₂(acac)₂ as Catalyst Precursor^a

element	binding energy (eV)	atomic % ^b	assignment ^c	ref
Mo 3d _{5/2}	228.7	0.70	Mo ⁴⁺ as in MoS ₂	30–31
S 2p	162.5	1.32	S ²⁻ as in MoS ₂	32
	164.2	1.69	organic sulfur	
C 1s	284.6	91.97	adventitious carbon	32
N 1s	399.5	1.47	organic nitrogen	32
O 1s	532.8	2.70	organic oxygen	32
	530.0			
V 2p _{3/2}	517.7	0.11	V ⁴⁺ as in V ₂ O ₅	32

^a The reactions were carried out in a 300 mL batch reactor at 410 °C, 250 ppm of metal, 11 MPa of final pressure of methane for a 1 h period. The coke was isolated by filtration after diluting the upgraded crude oil in toluene. ^b Atomic percentage on the surface. ^c Most probable assignment according to the published literature.^{30–32}

An experiment (Table 2, run 3) conducted under hydrogen atmosphere afforded an upgraded product with slightly better properties (15° API, 22% HDS, 65% conversion of >500 °C fraction and 6.5% coke) than those obtained under methane (run 1) and argon (run 2) atmospheres. Thus, the order of reactivity is H₂ > CH₄ > N₂ as found by Ovalles et al.^{11,12} and Sundaram¹⁴ for thermally activated processes. Also, similar order of reactivity was reported by Egiebor and Gray in their iron-catalyzed coal liquefaction experiments¹⁶ and Ovalles et al. for Mo–Ni/Al₂O₃-catalyzed extra-heavy crude oil upgrading.¹³

From the methane-upgrading reaction using MoO₂-(acac)₂ as dispersed catalyst, the coke formed was characterized by EDAX, XPS, and electron microscopy. X-ray diffraction and XPS analyses showed the presence of molybdenum and sulfur.^{28,29}

Furthermore, the binding energy for the Mo(3d_{5/2}) was found (Table 3) at 228.7 eV and can be assigned to Mo⁴⁺ according to the data reported in the literature.^{30,31} Additionally, two sulfur species were detected in the S(2p) region at 162.5 and 164.2 eV which can be assigned to S²⁻ and organic sulfur, respectively.³²

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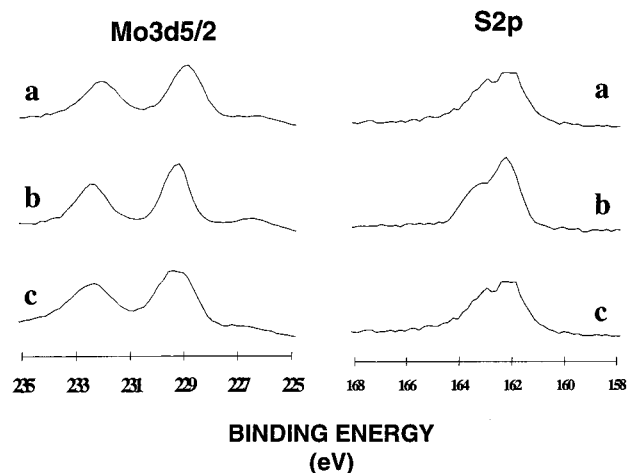


Figure 2. XPS spectra in the Mo(3d_{5/2}) and S(2p) regions of (a) MoS₂ prepared on a molybdenum sheet; (b) MoS₂/Mo reacted with 0.3 MPa of CH₄ at 420 °C for 2 h; (c) MoS₂/Mo reacted with 0.3 MPa of CH₄ at 420 °C for 2 h followed by Ar⁺ etching for 15 min.

The ratio of the atomic percentages of Mo⁴⁺ (0.7) and S²⁻ (1.32) is 0.53 which corresponds very well with the stoichiometry of MoS₂ (Table 3) as reported previously by Fixari et al.⁶ The formation of MoS₂ is believed to occur by in situ reaction with sources of sulfur in the reaction mixture during the methane upgrading reaction as discussed previously in the Introduction.^{1–9}

In the next section, detailed mechanistic studies are presented using MoS₂ synthesized on a pure molybdenum sheet. Also, upgrading experiments using ¹³CH₄ and CD₄ are discussed and the most probable mechanism for methane activation is proposed.

Mechanistic Studies. In order to gain mechanistic information, a sample of MoS₂ was synthesized on a pure molybdenum sheet following a known procedure³³ and was characterized by XPS as shown in Figure 2a. The values found for Mo(3d_{5/2}) (228.8 eV) and for S(2p) (162.2 eV) corresponded very well with those reported in Table 3 and in the literature.^{30–32}

The MoS₂/Mo sample was reacted with 2.7 atm of ¹²CH₄ at 420 °C for 2 h followed by Ar⁺ etching for 15 min with little changes in the XPS spectra of the Mo and S as shown in Figure 2b,c, respectively. These results indicate that the MoS₂ layer supported on the Mo sheet is very stable under the reaction conditions used in this work.

Secondary ion mass spectrometry analysis (SIMS) in the 10–20 *m/e* region of the MoS₂/Mo sample was carried out and the results are presented in Figure 3a. As can be seen, steady-state concentration of adsorbed CH_x moieties presented a normal isotope carbon distribution with the highest peak centered at 12 *m/e* with lower components at 13, 14, and 15 *m/e*.

For the reaction of the MoS₂/Mo sample with ¹²CH₄ at 420 °C for 2 h, a different carbon distribution was obtained (Figure 3b) having the most intense peak at 15 *m/e*. These carbon species were totally removed after Ar⁺ etching for 15 min (Figure 3c), indicating they are adsorbed on the surface of the MoS₂/Mo sample. These results indicate that MoS₂ were reacting with methane

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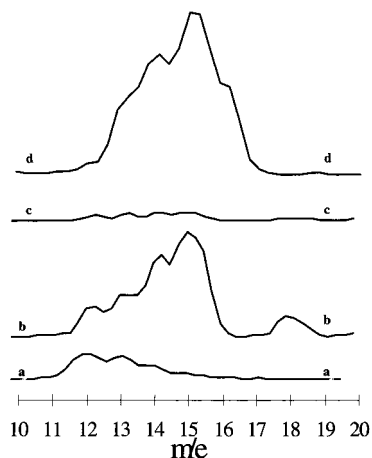
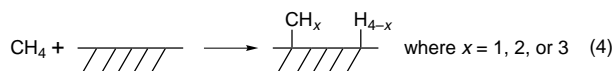


Figure 3. Secondary ion mass spectrometry in the 10–20 m/e region of (a) MoS_2 prepared on a molybdenum sheet; (b) MoS_2/Mo reacted with 0.3 MPa of $^{12}\text{CH}_4$ at 420 °C for 2 h; (c) MoS_2/Mo reacted with 0.3 MPa of $^{12}\text{CH}_4$ at 420 °C for 2 h followed by Ar^+ etching for 15 min; (d) MoS_2/Mo reacted with 0.3 MPa of $^{13}\text{CH}_4$ at 420 °C for 2 h.

at reaction conditions yielding carbon species (CH_x , where $x = 1, 2$, or 3) attached to the catalyst surface. According to the SIMS spectra shown, methyl groups ($x = 3$) were found to be the most abundant fragment.

In order to confirm that the CH_x moieties were coming only from methane decomposition reactions and not from another different source (such as chamber contamination and/or drybox sample manipulation, etc.), an additional experiment with $^{13}\text{CH}_4$ was carried out and the SIMS spectra are shown in Figure 3d. As can be seen, a shift to heavier masses of the carbon species adsorbed on the MoS_2 surface was observed and a peak at 16 m/e (attributed to adsorbed $^{13}\text{CH}_3$) was detected which was not present in the previous $^{12}\text{CH}_4$ -containing experiment (Figure 3b). These results (XPS and SIMS) strongly indicate that MoS_2 catalyst is involved in the methane activation step and that adsorbed CH_x species (where $x = 1, 2$, or 3) are concurrently generated.

From theoretical³⁴ and experimental results,³⁵ it was proposed that methane can be activated by a sulfided metal catalyst (MoS_2), generating hydrogen and CH_x groups adsorbed on the surface (eq 4) as demonstrated by the SIMS spectra.



For $\text{MoO}_2(\text{acac})_2$ soluble catalyst, an increase (16.7%) in the amount of α -hydrogen bonded to aromatic rings was observed as determined by ^1H NMR (Table 4), in comparison with those observed for the control run (14.7%) and for the crude oil (15.5%). Similar catalytic runs carried out under argon and hydrogen atmospheres and $\text{MoO}_2(\text{acac})_2$ led to lower amount of α -hydrogen bonded to aromatic rings (11.6 and 11.1% for Ar- and H_2 -containing experiments, respectively) than that found in the CH_4 -containing experiment (16.7%).

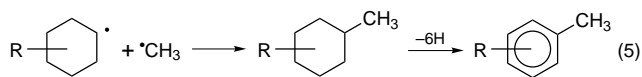
Also, an intense aromatization occurred for all the upgrading reactions as shown by the increase in the

Table 4. Protons Distributions for Upgraded Hamaca Crude Oil Measured by ^1H NMR Using $\text{MoO}_2(\text{acac})_2$ as Catalyst Precursor^a

run	gas used	H_{arom}^b	$\text{H}_{\text{aliph}}^c$	H_α^d	H_β^e	H_γ^f
Hamaca crude oil		5.1	94.9	14.7	56.2	24.0
control ^g	CH_4	9.0	91.0	15.5	52.0	23.5
1	CH_4	8.3	92.0	16.7	50.9	23.8
2	argon	7.6	92.4	11.6	57.3	23.5
3	H_2	10.0	90.0	11.1	56.2	22.7

^a The reactions were carried out in a 300 mL batch reactor at 410 °C, 250 ppm of Mo, 11 MPa of final pressure for a 1 h period. The results are the average of at least two different reactions. acac = acetylacetonate. ^b H_{arom} = hydrogen bonded to aromatic carbons. ^c H_{aliph} = hydrogen bonded to aliphatic carbons. ^d H_α = hydrogen bonded to aliphatic carbons in α position to an aromatic ring. ^e H_β = hydrogen bonded to aliphatic carbons in β position to an aromatic ring. ^f H_γ = hydrogen bonded to aliphatic carbons in γ or more position to an aromatic ring. ^g Control experiment, i.e., no catalyst was used.

percentages of aromatic protons from 5.1% in the original crude to approximately 10% for runs 1–3. These results can be rationalized by incorporation of the adsorbed CH_x groups (eq 4) to the crude oil molecules, as shown in eq 5 for $x = 3$.



where R = hydrocarbon (aliphatic or aromatic).

Naphthenic radicals shown in eq 5 can be generated by either thermal or catalytic breaking of C–H bond under the reaction temperature (410 °C). Egiebor and Gray found methyl and dimethyl products by GC analysis of the donor solvent (tetralin), which was attributed to direct alkylation by reaction with methane in their iron-catalyzed coal liquefaction experiments.¹⁶ Also, similar results were obtained previously for extra-heavy crude oil upgrading under thermal conditions.¹² The incorporation of CH_x species into the crude oil molecules was confirmed by isotopic carbon distribution measurements ($^{13}\text{C}/^{12}\text{C}$) and the results will be discussed in the next section.

On the other hand, adsorbed hydrogen generated by eq 4 could be available for sulfur removal^{13,16} and for hydrogenation of asphaltenes¹⁶ (lower coke production) with the concomitant crude oil upgrading. This suggestion was confirmed by mass spectrometry, in which (H)(D)S (at 35 m/e) and D_2S (at 36 m/e) were detected in the gas phase of the CD_4 -containing experiment (Figure 4,a and b), giving additional evidence in favor of the methane activation reaction outline in eq 4.

Extent of Methane Incorporation. The determination of the extent of methane incorporation to the crude oil using molybdenum-dispersed catalysts proved to be a difficult task mainly because the amount of CH_4 added to the upgraded hydrocarbon was very small.¹³ Attempts to determine it by D and ^{13}C NMR spectroscopy was unsuccessful and only a maximum value of 1% w/w could be estimated due to the relatively low sensitivity of these techniques. For comparison purposes, the values of hydrogen consumed in commercial residue upgrading processes such as INTEVEP's HDH, CANMET, and Texaco's H-OIL are reported to be 2% w/w, approximately.³⁶

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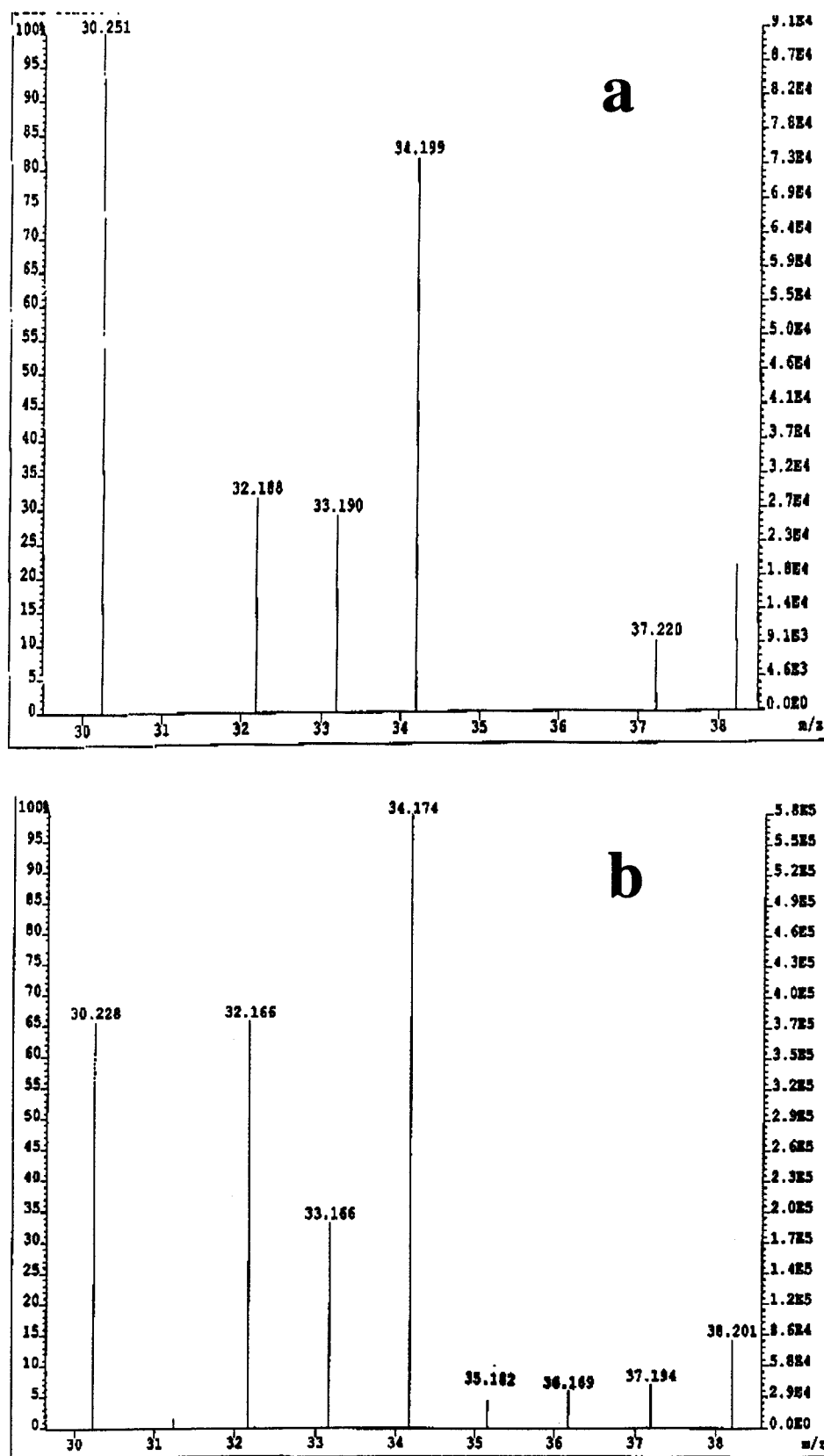


Figure 4. Mass spectrometry analysis of the gas samples after upgrading of Hamaca extra-heavy crude oil: (a) using CH_4 ; (b) CD_4 . Same conditions as Table 2.

For $\text{MoO}_2(\text{acac})_2$ soluble catalyst, an increase in the percentage of hydrogen in the upgraded product was observed (Table 5, 10.6%) in comparison with the original crude oil (9.5%). As mentioned in the Experimental Section, the amount of gases produced was very

small (<10%) and therefore the percentage of hydrogen added to the upgraded Hamaca crude can be estimated to be 1.1% w/w, approximately. This value is in the same order of magnitude as those reported for commercial processes such as HDH, H-Oil, etc. mentioned

Table 5. Elemental and Carbon Isotope Analysis for Upgraded Hamaca Crude Oil^a

run	gas used	% C	% H	% N	% S	% O ^b	$\delta^{13}\text{C}^c$
Hamaca crude oil		82.50	9.50	0.70	3.40	3.90	-27.89
1	¹² CH ₄	85.30	10.25	0.52	2.87	1.03	-27.30
3	H ₂	85.60	10.60	0.65	2.64	0.51	
4	¹³ CH ₄	85.60	10.10	0.55	2.90	0.85	-27.03

^a The reactions were carried out in a 300 mL batch reactor at 410 °C, 250 ppm of Mo, 11 MPa of final pressure for a 1 h period. The results are the average of at least two different reactions.

^b Determined by balance to 100%. ^c $\delta^{13}\text{C} (\pm 0.05) = [(^{13}\text{C}/^{12}\text{C})_{\text{sample}} / (^{13}\text{C}/^{12}\text{C})_{\text{standard}} - 1] \times 1000$. The ¹³C/¹²C ratios were determined by mass spectrometry.

before.³⁷ Therefore, lower values for methane addition were expected due to the lower reactivity of CH₄ in comparison with H₂.

In order to determine the amount of methane incorporated into the crude oil, carbon isotope ratio mass spectrometry analysis was carried out using a static combustion method as reported in the literature.^{25,26} The ¹³C/¹²C ratios of the CO₂ produced in parts per thousand with respect to a standard (PDB) were determined ($\delta^{13}\text{C}$) and the results are shown in Table 5. For the reaction with ¹²CH₄ (run 1), a slightly increase (less negative) in the $\delta^{13}\text{C}$ value was found (-27.30‰) in comparison with the original crude oil (-27.89‰).

Similar results were reported by Fixari et al. in the hydroconversion of Safaniya crude oil in the presence of a molybdenum catalyst.³⁷ These authors found an increase (less negative) in the $\delta^{13}\text{C}$ value from -26.95‰ in the original crude oil to -26.20‰ in the upgraded sample.³⁸ The observed increase in the amount of ¹³C was attributed to the reported difference in C-C bond breaking, since ¹²C-¹²C bonds are easier to cleave than ¹³C-¹²C bonds by a factor of 4%.^{37,38}

For the ¹³CH₄-containing experiment (run 4), a further increase in the $\delta^{13}\text{C}$ value (from -27.30‰ to -27.03‰) was observed in comparison with the reaction with ¹²CH₄. This result gives conclusive evidence that methane was incorporating into the upgraded crude oil as discussed in the previous sections.

Subtracting the amount of ¹³C increased by cracking reaction (run 1) from the ¹³CH₄-containing experiment (run 4), the amount of CH₄ addition to the crude can be estimated as 0.01% w/w, which is 2 orders of magnitude

lower than that found for H₂ addition where the hydrogen source was H₂ (run 3). This value confirms the early estimates using by D- and ¹³C NMR spectroscopy as mentioned before and is in agreement with the very well known difference in chemical reactivity between the H₂ and the CH₄ molecules.

Finally, the fact that the upgrading of extra-heavy crude oil is enhanced in the presence of MoO₂(acac)₂ (as shown before) seems to indicate that methane is being activated exclusively by the metal catalyst and then incorporated into the hydrocarbon molecules. However, the role of the thermal processes (i.e., chain propagation of radicals, eq 1-3) and the amount of CH₄ incorporated by this pathway cannot be neglected at the present time and deserves to be investigated in detail in the future.

Conclusions

1. The reaction of Hamaca extra-heavy crude oil in the presence of MoO₂(acac)₂ as dispersed catalyst at 11 MPa of methane as a source of hydrogen and 410 °C for 1 h led to an increase of 7° in the API gravity of the upgraded product, 16% reduction in sulfur content, and 55% conversion of the >500 °C fraction with respect to the original crude. Based on spectroscopic data, it was confirmed that molybdenum is present as MoS₂ and dispersed in the coke particles.

2. By XPS, ¹H NMR, MS, and SIMS experiments, a mechanism for the methane addition to the crude oil can be proposed which involves activation of CH₄ by the MoS₂ catalyst generating CH_x and H_{4-x} species on the catalyst surface. The CH_x moiety can be added to the hydrocarbon molecules forming methylated products. The H_{4-x} species could be available for sulfur removal and for hydrogenation of asphaltenes (lower coke production).

3. By carbon isotope ratio mass spectrometry analysis, an increase in the $\delta^{13}\text{C}$ value was observed for the ¹³CH₄-containing experiment in comparison with the reaction with ¹²CH₄. This result gives conclusive evidence that methane is incorporating to the upgraded crude oil molecules with an estimated value of 0.01% w/w.

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