



# Use of a dispersed iron catalyst for upgrading extra-heavy crude oil using methane as source of hydrogen<sup>☆</sup>

Cesar Ovalles<sup>a,\*</sup>, Eduardo Filgueiras<sup>a</sup>, Alfredo Morales<sup>a</sup>, Carlos E. Scott<sup>b</sup>,  
Fernando Gonzalez-Gimenez<sup>c</sup>, B. Pierre Embaid<sup>c</sup>

<sup>a</sup>PDVSA-INTEVEP, Apdo. 76343, Caracas 1070A, Venezuela

<sup>b</sup>Centro de Catálisis, Petróleo y Petroquímica, Facultad de Ciencias, Universidad Central de Venezuela, Apdo. 47102, Caracas 1040A, Venezuela

<sup>c</sup>Departamento de Física, Ciencias, UCV, Apdo. 47586, Caracas 1041A, Venezuela

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## Abstract

The use of an iron dispersed catalyst, derived from  $\text{Fe}_3(\text{CO})_{12}$ , for extra-heavy crude oil upgrading using methane as source of hydrogen was studied. The upgrading reactions were carried out batchwise in a stainless-steel 300 ml Parr reactor with 250 ppm of Fe at a temperature of 410–420 °C, a pressure of 11 MPa of  $\text{CH}_4$ , and a residence time of 1 h. In the presence of  $\text{Fe}_3(\text{CO})_{12}$ , the reaction of Hamaca extra-heavy crude oil led to a reduction of two orders of magnitude in the viscosity (from 500 to 1.3 Pa s), 14% reduction in sulfur content, and 41% conversion of the > 500 °C fraction in the upgraded product with respect to the original crude. The iron catalyst was isolated from the coke produced from the upgrading reaction and was analyzed by XPS, EDAX, and Mössbauer spectroscopy. The results indicated the presence of a Fe–V mixed sulfide species with a composition ca.  $(\text{Fe}_{0.6}\text{V}_{0.4})_z\text{S}$ , where  $z$  is in the range 0.8–0.9.

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## 1. Introduction

The use of natural gas (methane) as a hydrogen source for the upgrading of extra-heavy crude oil [1–6] and coal [7–16] has been the subject of several studies during the last few years. In particular, the reaction of Hamaca crude oil ( $^{\circ}\text{API} = 8.3$ ) under thermal conditions (380 °C, 11.0 MPa of  $\text{CH}_4$  for 4 h residence time) and in the presence of water as additive, led to a decrease of two 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% of reduction of sulfur with respect to the original crude [1–3]. By  $^1\text{H}$  and  $^2\text{D}$  NMR analysis, the most probable pathway is a free-radical mechanism, which involves incorporation of methane via production of methyl radicals [3].

Using an alumina supported molybdenum–nickel catalyst and at similar conversion of the > 540 °C fraction, a

relatively higher percentage of desulfurization (28%) and lower percentage of asphaltenes (9.3%) was obtained than those found in thermal reactions (11 and 11.8%, respectively) [1,4]. These results indicate that methane can be catalytically activated and used for upgrading extra-heavy crude oil. Furthermore, using a dispersed molybdenum catalyst, derived from  $\text{MoO}_2(\text{acac})_2$  (where acac is acetylacetonate) and 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  $\text{CH}_4$  in the extra-heavy crude oil upgrading process [5,6].

In this work, we studied the use of a dispersed iron catalyst, derived from  $\text{Fe}_3(\text{CO})_{12}$  for extra-heavy crude oil upgrading using methane as source of hydrogen. The characterization of the upgraded products by  $^1\text{H}$  NMR were carried out in order to gain mechanistic information regarding the methane activation processes that are occurring during the crude oil upgrading reactions. Also, the coke produced was characterized by TEM, EDAX, XPS, and Mössbauer spectroscopy in order to determine the iron species present during upgrading reactions.

\* Corresponding author. Tel.: +58-2129086991; fax: +58-2126087642.

E-mail address: [ovallesc@pdvsa.com](mailto:ovallesc@pdvsa.com) (C. Ovalles).

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## 2. Experimental part

The crude oil employed in this work came from the Hamaca oil field in the Orinoco Belt and its analysis is as follows: API gravity at 15.6 °C = 8.7, water ≤ 1 w/w%, H/C wt ratio = 0.115, sulphur = 3.40 w/w%, nickel = 91.9 ppm, vanadium = 412 ppm, asphaltenes = 12.5 w/w%, percentage of residue (500 + °C) = 57%, viscosity at 30 °C = 500 Pa s.

Transmission electron microscopy (TEM) analyses were carried out in an ISI equipment model SS-40 coupled with an EDAX X-ray analyzer model 9100. The samples were covered with gold to improve contrast.

X-ray photoelectron spectroscopic (XPS) experiments were carried out using a Leybold–Heraeus surface analysis system, which was operated with an aluminium 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 Pentium IBM compatible computer. The instrument sensitivity factors used for scaling the photoelectron peak areas were calculated using the method reported by Leon and Carrazza [18].

The Mössbauer spectroscopy was carried out at room temperature, with a constant acceleration spectrometer, in the triangular symmetric mode for the velocity. The source was a <sup>57</sup>Co in palladium.

The upgrading reactions were carried out batchwise in a stainless-steel 300 ml Parr reactor with 250 ppm of Fe (as Fe<sub>3</sub>(CO)<sub>12</sub>) at a temperature of 410–420 °C, a pressure of 11 MPa of the gas used (CH<sub>4</sub>, N<sub>2</sub> or H<sub>2</sub>) with a residence time of 1 h as described elsewhere [5,6]. The coke formed during the upgrading reactions was isolated by adding toluene (10:1 by weight) followed by centrifugation at 3000 rpm for 20 min. The last procedure was repeated once more and, after filtration using a medium size fritted glass, the solid was dried at 75 °C for 2 h. The isolated coke was analyzed by TEM, EDAX, XPS and Mössbauer spectroscopy.

The percentages of volatile material in the upgraded crude oil were determined by the method reported by Ceballos and coworkers using a Hewlett-Packard gas

chromatograph, model 5880 [17]. The percentage of conversion of the residue >500 °C (w/w) with respect to the feed was defined elsewhere [3,5,6].

## 3. Results and discussion

### 3.1. Upgrading reactions

The reaction of Hamaca extra-heavy crude oil (Table 1) at 11 MPa of methane and 410 °C for 1 h (Table 1, control run) led to a reduction of two orders of magnitude in the viscosity (from 500 to 2 Pa s), 10% of reduction in sulfur content and 41% conversion of the >500 °C fraction in the upgraded product with respect to the original crude. Analogous reaction carried out in the presence of Fe<sub>3</sub>(CO)<sub>12</sub> as dispersed catalyst (Table 1, run 1) yielded a product with further reduction in the viscosity (1.3 Pa s), higher reduction in sulfur content (14%) and similar value of conversion of the heavy fraction (40%). These results (higher HDS% and lower viscosity) indicate that the presence of the iron catalyst is necessary to further enhance the upgrading of extra-heavy crude oil in the presence of methane. Even though the activity of the dispersed catalyst is not very high compared with their thermal counterpart, the observed upgrading on the produced crude oil is clearly above the experimental errors of the analytical techniques used (see Table 1).

A reaction carried out in an inert nitrogen atmosphere (Table 1, run 2) yielded a product with higher viscosity (2.7 Pa s), less reduction of sulfur content (8%) and lower conversion of the >500 °C fraction (36%) with respect to the methane containing experiment (Table 1, run 1). These results may indicate that methane can be activated by metal catalysts and is probably involved as a source of hydrogen in the upgrading reaction.

An experiment (Table 1, run 3) conducted under hydrogen atmosphere afforded an upgraded product with slightly better properties (1.2 Pa s, 22% HDS, 40% conversion of >500 °C fraction and 5% coke) than those obtained

Table 1  
Upgrading of extra-heavy crude oil using Fe<sub>3</sub>(CO)<sub>12</sub> as organometallic precursor

Run	Gas used	HDS <sup>a</sup> (wt%)	% Conversion >500 °C <sup>b</sup>	Viscosity (Pa s) <sup>c</sup>	Coke (wt%) <sup>d</sup>	Gases (wt%) <sup>d</sup>	Liquids (wt%) <sup>d</sup>
Hamaca crude oil	–	(3.40% S)	–	(500)	–	–	–
Control <sup>e</sup>	CH <sub>4</sub>	10.0	41.0	1.99	7.7	4.6	87.7
1	CH <sub>4</sub>	14.2	40.5	1.34	6.9	4.6	88.5
2	N <sub>2</sub>	8.1	35.8	2.77	7.0	3.1	89.9
3	H <sub>2</sub>	22.0	39.7	1.20	5.0	4.5	90.5

The reactions were carried out in a 300 ml batch reactor at 410 °C, 250 ppm of Fe, 11 MPa of final pressure for a 1 h period. The results are the average of at least two different reactions and errors are expressed in terms of the standard deviations.

<sup>a</sup> Percentage of desulfurization with respect to the starting crude oil (±1%).

<sup>b</sup> Percentage of conversion of the residue >500 °C (w/w) with respect to the feed as defined in Ref. [3], 5–6 (±2%).

<sup>c</sup> Viscosity measured at 30 °C (±0.2 Pa s).

<sup>d</sup> Percentage with respect of the product at the end of run (±2%).

<sup>e</sup> Control experiment, i.e. no catalyst was used.

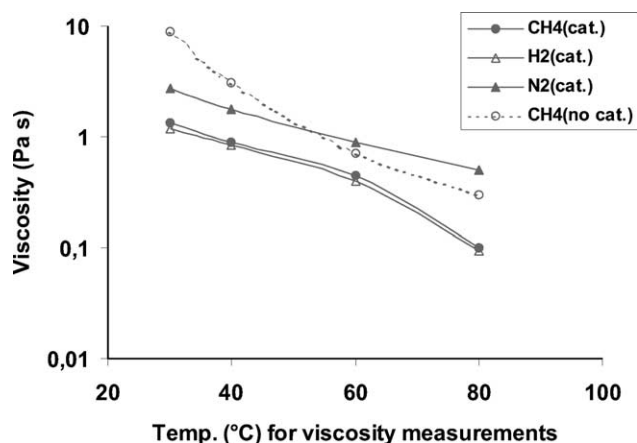
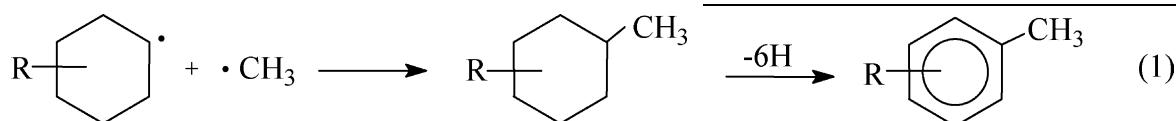


Fig. 1. Effects of the nature of the gas used on the viscosity of upgraded Hamaca crude oil. (○) Methane, (△) hydrogen and (▲) nitrogen. Same conditions as Table 1.

under methane (run 1) and nitrogen (run 2) atmospheres. Furthermore, the effects of the nature of the gas used on the viscosity of the upgraded Hamaca crude oil can be seen in Fig. 1. Higher viscosities were obtained for the reaction under nitrogen than those found with hydrogen and methane with or without catalyst. Thus, the order of reactivity is  $H_2(\text{cat.}) > CH_4(\text{cat.}) > CH_4 > N_2(\text{cat.})$  as reported by Ovalles et al. [3] and Sundaram [7,8] for thermally activated processes and by Egiebor and Gray in iron catalyzed coal liquefaction experiments [10] and Ovalles et al. for Mo–Ni/ $Al_2O_3$  catalyzed extra-heavy crude oil upgrading [4,6].

In order to gain mechanistic information for the upgrading reactions, H NMR analyses were carried out to the upgraded crude oil and the results are shown in Table 2. For  $Fe_3(CO)_{12}$  soluble catalyst, an increase (17.2%) in the amount of  $\alpha$ -hydrogen bonded to aromatic rings was observed in comparison with those observed for the control run (14.7%) and for the crude oil (15.5%). Similar catalytic runs carried out under nitrogen and hydrogen atmospheres and  $Fe_3(CO)_{12}$  led to lower amount of  $\alpha$ -hydrogen bonded to aromatic rings (16 and 15% for  $N_2$  and  $H_2$  containing experiments, respectively) than that found in the  $CH_4$  containing experiment (17%).

Furthermore, an intense aromatization occurred for all the upgrading reactions as shown by the increase in the 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 methyl groups (or, in general,  $CH_x$  species where  $x = 1, 2,$  or  $3$ ) to the crude oil molecules, as shown in Eq. (1) [6].



where R = hydrocarbon (aliphatic or aromatic).

Naphthenic radicals shown in Eq. (1) can be generated by either thermal or catalytic breaking of C–H bonds under

Table 2

Protons distributions for upgraded Hamaca crude oil measured by  $^1H$  NMR using  $Fe_3(CO)_{12}$  as catalyst precursor

Run	Gas used	$H_{\text{arom}}^a$	$H_{\text{aliph}}^b$	$H_{\alpha}^c$	$H_{\beta}^d$	$H_{\gamma}^e$
Hamaca crude oil	–	5.1	94.9	14.7	56.2	24.0
Control <sup>f</sup>	$CH_4$	9.0	91.0	16.2	52.0	23.5
1	$CH_4$	8.4	91.6	17.2	51.2	23.0
2	$N_2$	8.9	91.1	15.5	51.3	23.3
3	$H_2$	8.7	91.3	15.2	51.5	24.6

The reactions were carried out as described in Table 1. Errors are expressed in terms of the standard deviations ( $\pm 0.2\%$ ).

<sup>a</sup>  $H_{\text{arom}}$ : percentages of hydrogen bonded to aromatic carbons.

<sup>b</sup>  $H_{\text{aliph}}$ : percentages of hydrogen bonded to aliphatic carbons.

<sup>c</sup>  $H_{\alpha}$ : percentages of hydrogen bonded to aliphatic carbons in  $\alpha$  position to an aromatic ring.

<sup>d</sup>  $H_{\beta}$ : percentages of hydrogen bonded to aliphatic carbons in  $\beta$  position to an aromatic ring.

<sup>e</sup>  $H_{\gamma}$ : percentages of hydrogen bonded to aliphatic carbons in  $\gamma$  or more position to an aromatic ring.

<sup>f</sup> Control experiment, i.e. no catalyst was used.

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 [10]. Also, similar results were obtained previously for extra-heavy crude oil upgrading under thermal [3] and catalytic conditions [6]. The incorporation of  $CH_x$  species, coming from methane, into the crude oil molecules was confirmed by isotopic carbon distribution measurements ( $^{13}C/^{12}C$ ) using  $^{13}CH_4$  as a source of hydrogen [6].

Alternatively, the higher percentages of HDS obtained in the  $CH_4$  containing run in comparison with the nitrogen experiment (runs 1 and 2, Table 1) can also be explained due to the generation of hydrogen as shown in Eq. (1). As suggested by one of the referees, other possible mechanisms can be proposed such as direct addition of methyl radicals to aromatic moieties. Further studies are required to address these important questions.

### 3.2. Characterization of the produced coke

The coke formed during the methane upgrading reaction using  $Fe_3(CO)_{12}$  as dispersed catalyst, was isolated by filtration and characterized by TEM, EDAX, XPS and Mössbauer spectroscopy. A TEM photograph is shown in Fig. 2 and typical coke morphology can be

observed with no special features. An EDAX analysis (Fig. 3) showed the presence of iron and sulfur as the main components.



Fig. 2. Transmission electron microscopy photograph of the coke isolated from the  $\text{Fe}_3(\text{CO})_{12}$  containing upgrading reactions. Same conditions as Table 1.

After 1 h etching with  $\text{Ar}^+$  ions, XPS analyses showed the presence of iron, vanadium and sulfur [19–21]. The binding energies for the Fe 2p<sub>3/2</sub> and V 2p<sub>3/2</sub> were found (Table 3) at 707.4 and 517.4 eV, respectively. According to the data reported in the literature, these bands can be assigned to iron and vanadium present in a sulfide structure [19–24]. Additionally, a sulfur specie was detected in the S 2p region at 161.3 eV, which can be assigned to  $\text{S}^{-2}$  [21–24].

The ratio of the atomic percentages of iron (0.54) and sulfur (1.31) is 0.53, which is lower than that (1.1–1.4) reported by Reucroft and coworkers [19] and for the expected FeS phase. To determine which type of Fe species were present, a Mössbauer study was undertaken.

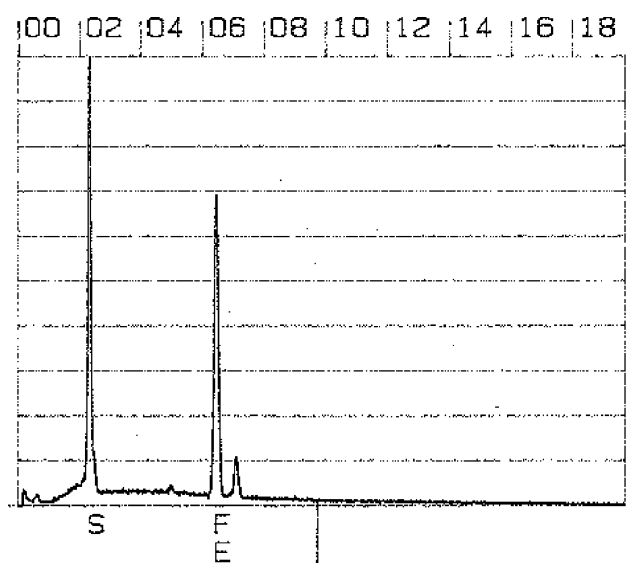


Fig. 3. X-ray diffraction analysis of  $\text{Fe}_3(\text{CO})_{12}$  derived catalyst isolated from coke.

Table 3

Results of the XPS analysis of the coke isolated from upgraded Hamaca crude oil using  $\text{Fe}_3(\text{CO})_{12}$  as catalyst precursor after 1 h etching with  $\text{Ar}^+$  ions

Element	Binding energy (eV)	at.% <sup>a</sup>	Assignment <sup>b</sup>	Reference
Fe 2p <sub>3/2</sub>	707.4	0.54	Fe in Sulfide	[18–20]
V 2p <sub>3/2</sub>	517.4	0.02	V in Sulfide	[20–23]
S 2p	161.3	1.31	$\text{S}^{-2}$	[20–23]
C 1s	284.6	97.20	Adventitious carbon	[20]
O 1s	532.8	0.91	Organic oxygen	[20–23]

The reactions were carried out as described in Table 1. The coke was isolated by filtration after diluting the upgraded crude oil in toluene.

<sup>a</sup> Atomic percentage on the surface.

<sup>b</sup> Most probable assignment according to the published literature.

The recorded spectrum is shown in Fig. 4A with the continuous line representing the result of a computer adjustment, which included, isomer shift (IS), quadrupole splitting (QS). A hyperfine field distribution histogram is

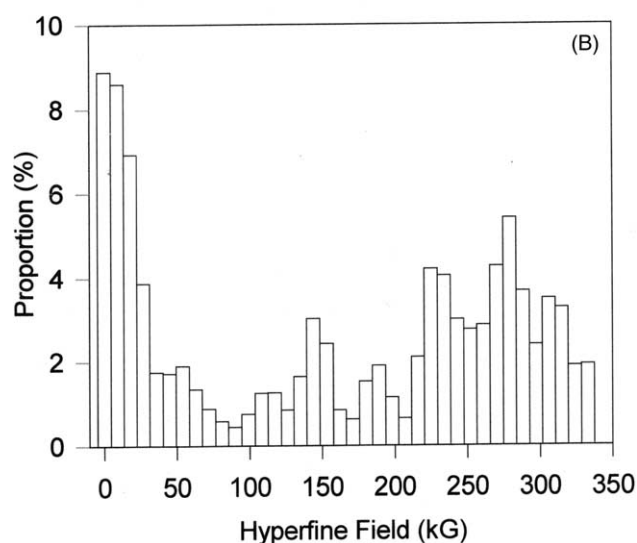
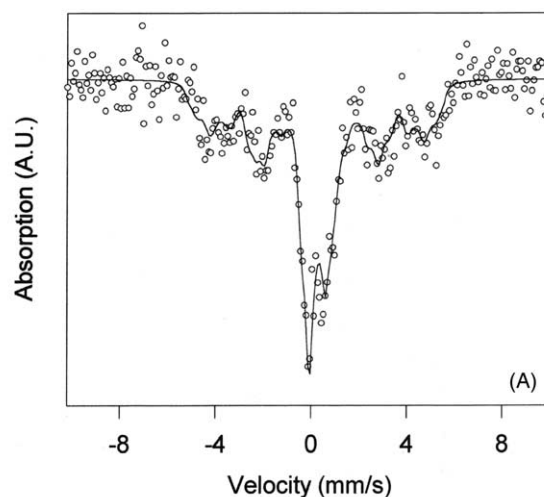


Fig. 4. (A) Mössbauer spectrum with the continuous line representing the result of a computer adjustment including, IS, FWHM and QS; (B) histogram for the hyperfine field distribution for the Mössbauer spectrum.

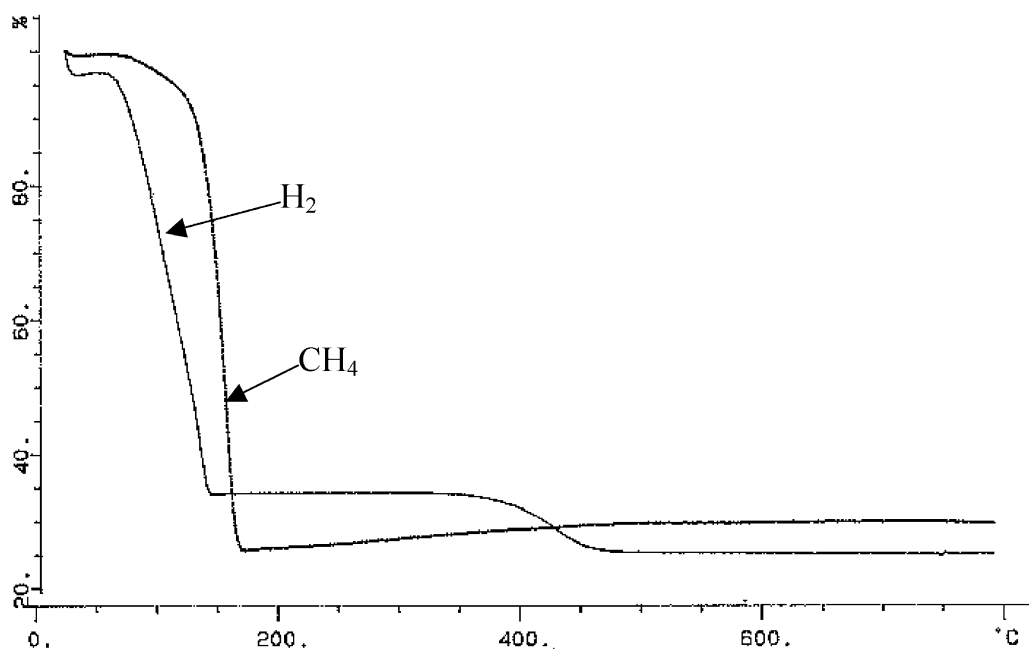
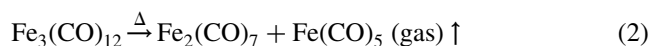


Fig. 5. Thermogravimetric analysis of  $\text{Fe}_3(\text{CO})_{12}$  under methane and hydrogen flow ( $10^\circ\text{C}/\text{min}$ ).

also shown in Fig. 4B. Due to the small concentration of iron, the spectrum has a rather poor statistics. However, the histogram of the HPFD obtained indicates the presence of a Fe and V mixed sulfide as compared to previous results [23–25]. According to the systematic study of those sulfides [23–25], the composition of the detected mixed sulfide could be estimated to be  $(\text{Fe}_{0.6}\text{V}_{0.4})_z\text{S}$ , where  $z$  is in the range of 0.8–0.9.

The formation of Fe–V mixed sulfide phases are certainly achieved in situ, by decomposition of the iron carbonyl ( $\text{Fe}_3(\text{CO})_{12}$ ) and subsequently the reaction of sulfur and vanadium coming from the feedstock. A very similar mechanism, which demonstrated the appearance of those mixed-sulfides as the active phases, has been put in evidence in HDM reactions undertaken with clay catalysts (the precursor is  $\text{Fe}_2\text{O}_3$ ) acting on a Pao-X1 heavy crude from the Orinoco belt.

Additional evidence for the latter mechanism was found by thermogravimetry analysis. As it can be seen in Fig. 5, the iron carbonyl organometallic complex decomposes in the temperature range of  $100\text{--}200^\circ\text{C}$  under  $\text{H}_2$  or  $\text{CH}_4$  atmospheres. Theoretical weight loss of  $\text{Fe}_3(\text{CO})_{12}$  to yield iron metal can be calculated to be 67%. For both gases, the experimental value was found to be 74%, approximately. This difference can be attributed to the formation of  $\text{Fe}(\text{CO})_5$  (see Eq. (2)) which has a boiling point of  $103^\circ\text{C}$  under TGA analysis conditions.



Also, the formation of coke deposited on the sample of  $\text{Fe}_3(\text{CO})_{12}$  has to be taken into consideration as reported in the literature.

#### 4. Conclusions

- In the presence of  $\text{Fe}_3(\text{CO})_{12}$ , the upgrading reaction of Hamaca extra-heavy crude oil led to a reduction of two orders of magnitude in the viscosity (from 500 to 1.3 Pa s), 14% reduction in sulfur content, and 41% conversion of the  $>500^\circ\text{C}$  fraction in the upgraded product with respect to the original crude.
- Based on the experiments carried out under nitrogen and  $\text{CH}_4$  atmospheres and H NMR measurements, it can be proposed that methane is probably involved as a source of hydrogen in the upgrading reaction.
- The results of the characterization by XPS, EDAX, and Mössbauer spectroscopy of coke produced indicated the presence of FeS and a Fe–V mixed sulfide species with a composition ca.  $(\text{Fe}_{0.6}\text{V}_{0.4})_z\text{S}$ , where  $z$  is in the range 0.8–0.9.

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