Article

Processing and Recovery of Heavy Crude Oil Using an HPA-Ni Catalyst and Natural Gas

Persi Schacht-Hernández, Alma Delia Miranda-Olvera,* Federico Jiménez-Cruz, Oscar Morelos-Santos, José Luis García-Gutiérrez, and Roberto Quintana-Solórzano

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: To maintain economic profitability and stabilize fuel prices, refineries actively explore alternatives for efficiently processing (extra) heavy crude oils. These oils are challenging to process due to their complex composition, which includes significant quantities of asphaltenes, resins, and sulfur and nitrogen heteroatoms. A critical initial step in upgrading these oils is the hydrogenation of polyaromatic compounds, requiring substantial hydrogen sources. Methane from natural gas streams is known to act as an effective hydrogen donor. This study investigates the use of a heteropolyacid (HPA) catalyst modified with nickel and methane to enhance the quality of heavy crude oil with an initial 8.0°API (at 15.5 °C) and 2200 cSt viscosity (at 37.5 °C). After treatment in a batch reactor at 380 °C and 4.4 MPa for 2 h, the oil properties markedly improved: API gravity increased from 8.0 to 16.0 (at 15.5 °C), and kinematic viscosity reduced from 2200 to 125 cSt (at 37.5 °C). Additionally, there was a significant decrease in asphaltenes (from 38.7 to 16.4% by weight), sulfur (from 5.9 to 4.0% by weight), and nitrogen (from 971 to 695 ppm). This was accompanied by an increase in the volume of light distillates from 1.3 to 4.9%, and middle distillates from 8.8 to 21.0%. These results suggest that nickel-modified HPA catalysts, combined with methane as a hydrogen donor, are a promising option for upgrading heavy crude oils.
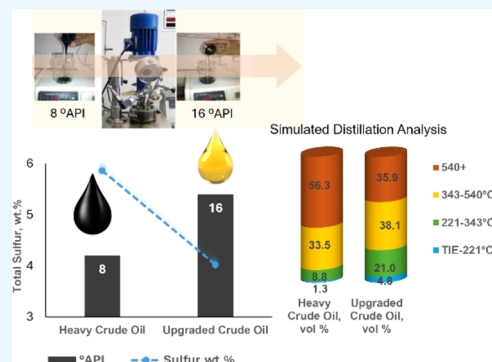
1. INTRODUCTION

Due to stringent environmental regulations related to contaminant content in automotive fuels and greenhouse gas (GHG) emissions, combined with a global trend toward reducing the carbon footprint of industrial activities, there is a pressing need to enhance the energy efficiency of processes involved in the exploitation, transportation, and conversion of crude oil. Paradoxically, the market inventory of heavier crude oils with larger carbon content is steadily increasing. This scenario is further complicated as some refineries, not originally designed to process these complex hydrocarbon streams, face significant challenges.[1,2] These challenges have spurred interest in intensifying the in situ upgrading of heavy crude oils to enhance their fluid properties directly at the reservoir, potentially meeting the quality specifications of existing refining centers and reducing crude transportation costs.[3,4]

Among the emerging technologies to improve the quality of heavy oil, the approach of in situ upgrading via catalyst injection stands out as a promising alternative.[3,5] This technology modifies the chemical structure of the crude oil components, thereby reducing viscosity and improving API gravity while simultaneously increasing the yield of valuable medium and light fractions at the expense of heavier ones. At the chemical reaction level, this technology facilitates the

hydrogenation of polyaromatic species to produce partially saturated aromatic compounds with attached saturated rings, which can transform into monocyclic aromatic compounds through a cracking mechanism.[6] A similar process occurs with the heteroatoms of sulfur and nitrogen in the oil, aiding in both hydrodesulfurization and hydrodenitrogenation. This reaction pathway requires a bifunctional catalyst: one function for the (partial) hydrogen saturation of refractory molecules and another for cracking the (partially) saturated species into lighter compounds. However, hydrogen is a scarce and an expensive gas and poses disadvantages[7,8] thus, alternative hydrogen sources are being explored. In this regard, hydrogen donors have emerged as a promising option for enhancing in situ heavy crude oil upgrading.[9−11] Notably, methane, with its high H-to-C ratio and large availability from (un)conventional natural gas sources, has been identified as a significant hydrogen donor for milder operating conditions compared to expensive molecular hydrogen under harsh conditions.[12−16]
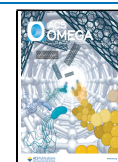
A key component for in situ heavy crude oil improvement is the catalyst, which can vary but often includes water-soluble, oil-soluble, mineral, ionic, and dispersed liquid forms. The catalyst must exhibit high activity and stability. Heteropolyacids (HPAs) are particularly suitable for methane activation due to their unique characteristics, including a high density of strong Brönsted-type acid sites, redox potential, thermal and solution stability, noncorrosiveness, and selectivity.[17−19] By incorporating metals into the HPA structure, highly active and selective bifunctional catalysts for hydrogenation and hydrocracking reactions can be produced.[20−22]

Previous studies on the upgrading of heavy crude oils using dispersed catalysts and hydrogen donors have shown promising results. For example, Ovalles et al. reported that an increase of up to 8° in API gravity (at 15.5 °C) and a 27% reduction in asphaltenes can be achieved using iron-containing nanocatalysts and tetralin processing an extra-heavy crude oil from the Orinoco Basin.[23] Ramos et al. observed a 22.7% increase in the content of aromatics using Co/MoS_2 nanocatalysts under specific conditions.[24] Other studies also reported a significant improvement in the quality of heavy crude combining various catalysts and experimental reaction conditions.[25−29]

With the depletion of light crude oil reserves, heavy and extra-heavy crude oils have become crucial for the refining to meet global energy demands. Traditional hydrocracking catalysts, typically consisting of supported metals, often deactivate due to the presence of high molecular mass compounds in the heavy crude oil. Thus, developing new nonsupported catalysts for transforming heavy crude into light hydrocarbons is essential.

Our research introduces by the first time the use of an $H_3PMo_{12}O_{40}$-Ni catalyst combined with addition of methane to improve the quality of a heavy crude oil. This heteropolyacid (HPA) catalyst modified with nickel combines HPA's strong acidic sites with nickel's catalytic properties. The result is a bifunctional catalytic system which, at the end, displays a high activity and selectivity for hydrogenation and hydrocracking reactions thus significantly enhancing the API gravity and viscosity of the crude oil under mild conditions. The use of methane as a hydrogen donor further boosts process overall efficiency.

2. EXPERIMENTAL SECTION

2.1. Preparation of the Catalyst.
The catalyst was prepared via hydrothermal synthesis in accordance with the following procedure: 20 g of hydrated phosphomolybdic acid ($H_3PMo_{12}O_{40}·xH_2O$, Sigma-Aldrich, > 99.99% purity based on trace metals analysis) was gradually added to 100 mL of distilled water maintained at 75 °C. The solution was stirred continuously with a magnetic agitator at 500 rpm until the phosphomolybdic acid fully dissolved and appeared translucent, approximately after 8 h. The solution was then cooled to room temperature (∼20 °C), and 40 g of nickel sulfate ($NiSO_4·6H_2O$, Sigma-Aldrich, > 99.99% purity based on trace metals analysis) was added. Stirring continued for 2 h at 500 rpm until a green solution formed. Solvent removal from this solution yielded a green powder solid.

2.2. Heavy Crude Oil Upgrading Reaction.
The upgrading reaction of heavy crude oil with an API gravity of 8.0° (at 15.5 °C) and kinematic viscosity of 2200 cSt at 37.5 °C (refer to Table 1) was conducted in a stainless-steel stirred batch reactor (Parr Instrument Company). This reactor

Table 1. Comparison of the Physical and Chemical Properties of Heavy Crude Oil and Upgraded Oil

property	heavy crude oil	upgraded oil	
		without catalyst	with HPA-Ni catalyst
API gravity, (at 15.5 °C)	8.0	14.0	16.0
kinematic viscosity, cSt			
15.6 °C	11,350	428	245
25 °C	5259	305	188
37.5 °C	2200	210	125
total sulfur, wt %	5.86	4.91	4.02
total nitrogen, ppm	971	754	695
SARA, wt %			
saturates	12.9	19.6	29.6
aromatics	23.5	31.7	35.6
resins	24.9	18.9	18.4
asphaltenes	38.7	29.8	16.4

configuration closely mimics the reactions occurring in oil reservoirs. Initially, the reactor was purged with nitrogen, pressurized to check for leaks, and then stabilized for further heating. For the catalytic process, a catalyst to oil mass ratio 200 was used, i. e., 200 g of heavy crude oil per gram of HPA-Ni catalyst, and then reacted at 380 °C and 4.4 MPa continuously stirring the reaction mixture at 1000 rpm for 2 h. Notably, the reactor was pressurized with natural gas comprising 94.3 vol % methane, which served as a hydrogen donor. Following the reaction, a thin layer of solid material that accumulated at the bottom of the reactor vessel was removed, washed with chloroform to extract any remaining hydrocarbons, weighed, and finally analyzed by X-ray diffraction (XRD) to identify the constituent species.

To isolate the specific effects of the catalyst on the quality and properties of the resultant products, a parallel experiment was conducted with heavy crude oil under the same conditions in the absence of any catalyst.

Methods for the characterization of the obtained products and the catalyst characterization are described in detail in the Supporting Information file.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Catalyst.
3.1.1. Elementary Analysis. Elementary analysis was done to confirm the bulk composition of the catalyst, specifically the content of nickel and molybdenum. The presence of these metals is crucial for the catalytic activity, providing both the acidic and metallic functions needed for the upgrading reactions. The bulk composition of the HPA-Ni catalyst was verified by Atomic Absorption Spectroscopy (AAS). The respective analytical results showed that the catalyst consisted of 16.1 wt % nickel (Ni) and 20.0 wt % molybdenum (Mo).

3.1.2. Potentiometric Titration. Potentiometric titration analysis was applied to determine the concentration and strength of the acid sites in the catalyst. Considering the complex chemical structure of the species composing the heavy crude oil (e.g., asphaltenes and polyaromatics), its conversion into smaller compounds requires a suitable catalytic formulation that involves the concomitant participation of two specific functions: (i) hydrogenation and (ii) cracking. Since the C−C bonds in condensed aromatic rings are essentially inert to the cracking function of the catalyst, they

need to be partially hydrogenated before cracking. The higher the catalyst acidity (i.e., density and strength), the faster the conversion of partially hydrogenated species, thus increasing the overall upgrading rate.

According to Figure S1, the initial acid strength of the catalyst is exceptionally high, with Ei reaching up to 800 mV. Most of the acid sites on the HPA-Ni catalyst can be classified as very strong, as indicated by signals up to 100 mV. The classification of acid strength based on Ei values is as follows: Ei > 100 mV for very strong sites, 0 < Ei < 100 mV for strong sites, −100 < Ei < 0 mV for weak sites, and Ei < −100 mV for very weak sites.[30] In the same figure, the signals range from 50 to 800 mV, corresponding to a total concentration of approximately 2.8 mequiv of *n*-butylamine per gram of solid.

3.1.3. Fourier Transform Infrared Spectroscopy (FTIR). The functional groups present in the catalyst and changes in its chemical structure were identified by FTIR spectroscopy. The characteristic absorption bands provide information about molecular interactions and the formation of new compounds. This information may result crucial for understanding the catalytic mechanism and the role of different functional groups in the reaction. In Figure S2 presents the FTIR spectra of the HPA-Ni catalyst. It displays four characteristic absorption bands attributed to the HPA-Ni structure ($[H_{3−x}PMo_{11}NiO_{40}]^{(4+x)}$) are observed at 1050 cm^{-1} ν(P-Oa), 966 cm^{-1} ν(Mo═Od), 864 cm^{-1} ν(Mo-Ob-Mo), 789 cm^{-1} ν(Mo-Oc-Mo).[31,32] Additionally, typical bands for the sulfate anion are noted at 1144 and 1105 cm^{-1}, along with bands corresponding to various phases of nickel sulfide at 1640 cm^{-1} (NiS, NiS$_2$), 1550 cm^{-1} (NiS, NiS$_2$), 1105 cm^{-1} (NiS, NiS$_2$), 908 cm^{-1} (NiS$_2$), 630 cm^{-1} (NiS, NiS$_2$, Ni$_3$S$_4$) are observed.[33] The broad band ranging from 3300 to 3500 cm^{-1} ν(O−H) is associated with water molecules within the secondary structure of the HPA-Ni.

3.1.4. X-ray Diffraction (XRD). XRD was used to identify the crystalline phases present in the catalyst and the solid residues recovered after the upgrading reaction. The XRD patterns indicated the formation of phases of active nickel sulfide, which are known to reduce the energy of the C−S and C−N bonds in sulfur and nitrogen heteroatoms.[34] This structural information is vital for correlating the catalyst composition with its performance in chemical reaction.

Figure 1a illustrates the XRD pattern of the as-synthesized HPA-Ni catalyst. Signal groups corresponding to two structural compounds were identified, which correspond to nickel sulfate and phosphomolybdic acid, catalogued under the JCPDS card numbers 01-079-0106 and 00-043-0317, respectively. The literature suggests that the X-ray diffractograms of HPA-Ni resemble those of $(NH_4)_3PMo_{12}O_{40}$,[34] where the Ni (II) ion occupies the counterion position in the polyoxometallate structure.

Figure 1b shows the XRD patterns of the thin layer of solid product collected from the bottom of the reactor after processing the heavy crude with the HPA-Ni catalyst. Predominantly, three different crystalline phases were observed specifically corresponding to nickel sulfides (NiS), (Ni$_3$S$_2$), and (Ni$_3$S$_4$), identified with the JCPDS card numbers 00-002-1443, 00-044-1418, and 01-076-1813, respectively.

The XRD pattern of this solid indicated the presence of crystalline phases corresponding to nickel sulfide, which is identified as the active phase of the catalyst.[35] This observation confirms that the sulfhydration step occurred during the upgrading reaction. According to previous reports and as was pointed out before, metallic sulfides can reduce the energy of
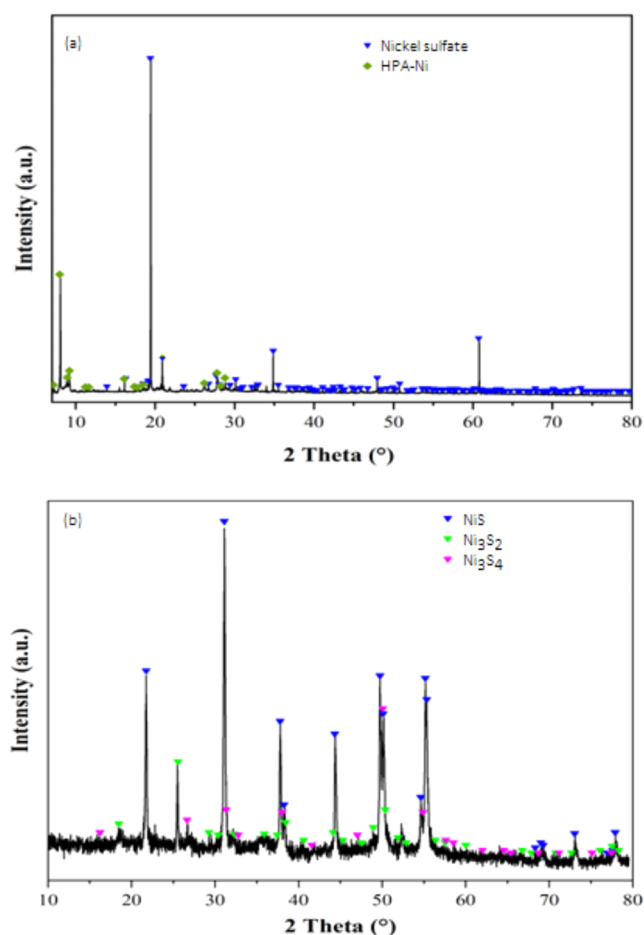

Figure 1. X-ray diffraction patterns: (a) HPA-Ni catalyst in its as-synthesized form; (b) solid recovered from the bottom of the reactor after processing.

the C−S and C−N bonds in sulfur and nitrogen heteroatoms,[36] which are known to be major contributors to the typical high viscosity of heavy crude oils.

3.1.5. Scanning Electron Microscopy (SEM). SEM images provide insights into the morphological characteristics of the catalyst, showing significant differences between the HPA and HPA-Ni samples. The lamellar structure with cubic shapes and visible cracks in the HPA-Ni catalyst indicates changes due to the proton exchange between HPA and nickel ions, which enhances its catalytic properties.

Figure 2 displays SEM images of the HPA and HPA-Ni catalysts, highlighting significant morphological differences between the two samples. Specifically, the phosphomolybdic acid (Figure 2a) exhibits a large, irregular shape with a rough surface. In contrast, the HPA-Ni catalyst (Figure 2b) features a lamellar structure with cubic shapes and some visible cracks. Probably, the observed changes in the surface morphology of the HPA-Ni catalyst are caused by a proton exchange between HPA and nickel ions aligning with findings of previous studies.[37,38]

3.2. Heavy Crude Oil Upgrading Reaction. *3.2.1. Total Acid Number and Total Basic Number.* The Total Acid Number (TAN) and Total Basic Number (TBN) were measured to quantify the acidity and basicity of the heavy crude oil and the upgraded product, respectively. These measurements reflect the concentration of acidic and basic compounds present in the oil. Typically, the oil refining
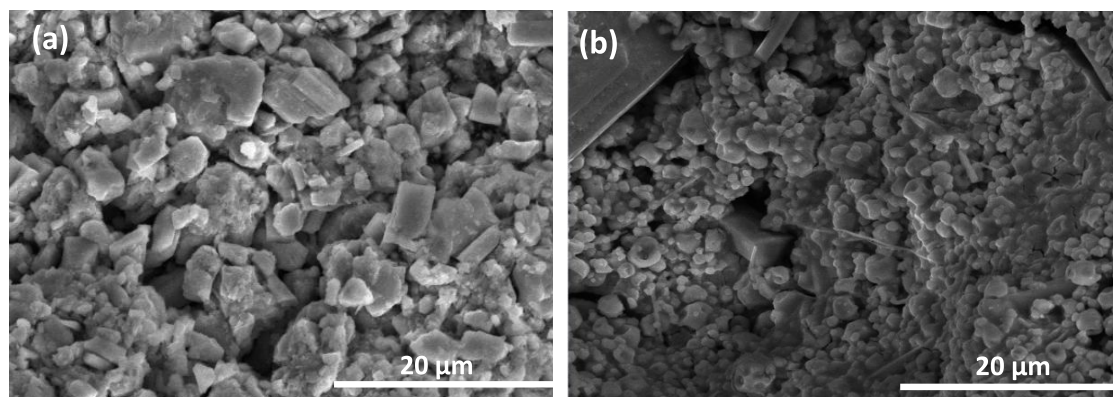
Figure 2. SEM Images: (a) HPA-Ni catalyst showing a lamellar structure with cubic shapes and cracks; (b) HPA catalyst characterized by a large, irregular shape and rough surface.

industry considers crude oil safe for processing if the TAN is below 0.5 mg KOH/g. However, Barth et al.[42] noted exceptions to this guideline. The TAN value indicates the amount of KOH required to neutralize the acids in the sample.[39−41]

Our analytical results indicated that the TAN and TBN values for the upgraded oil were lower than those of the heavy crude oil. Specifically, the TAN decreased from 1.6 mg KOH/g in the heavy crude to 0.76 mg KOH/g in the upgraded oil, and the TBN decreased from 3.38 to 2.64 mg KOH/g. These findings suggest that the acid−base balance plays a significant role in the overall acidity of crude oil. Identifying the specific functional groups contributing to this acidity is crucial for understanding how conjugated acids and bases influence the oil's properties. Moreover, lower crude oil recovery rates have been ascribed to higher TBN values, as reported by RezaeiDoust et al.[48]

3.2.2. Viscosity and API Gravity. Viscosity is a crucial parameter that determines the transportability of crude oil through pipelines to refineries.[42,43] Table 1 shows the values of the kinematic viscosity of oil products measured at three different temperatures for the heavy crude oil and the upgraded oil produced using both noncatalytic and catalytic reactions. For example, at 37.5 °C, the kinematic viscosity of the heavy crude was 2200 cSt, which reduced to 210 cSt with no catalyst and further decreased to 125 cSt using the HPA-Ni catalyst. This reduction is attributable to the formation of lower molecular mass species during the reaction, as also noted by Zhao et al.[3]

Significant changes were also observed in the API gravity after processing the heavy crude oil. Specifically, the API gravity (at 15.5 °C) increased from 8.0 to 14.0° following a noncatalytic reaction and further increased to 16.0 with the use of HPA-Ni catalysts. Bifunctional catalysts, which integrate metallic and acidic functions, enhance hydrocracking and hydrotreating reactions, and transform heavy unsaturated hydrocarbons into partially saturated, lighter, and less dense compounds. These transformations result in improved flow properties, as evidenced by an increased API gravity and a reduced viscosity. The upgraded oil showed an increased proportion of saturated hydrocarbons at the expense of unsaturated, polyaromatic species. This shift led to an increase in the H/C ratio, which is positively correlated with API gravity; in fact, a higher H/C ratio indicates a higher API.[44,45]

3.2.3. SARA Composition. The results of the SARA analysis (see Table 1) show that the heavy crude oil initially contained

12.9 wt % saturates, 23.5 wt % aromatics, 24.9 wt % resins, and 38.7 wt % asphaltenes. Following the upgrading reactions, both with and without a catalyst, the concentrations of saturates and aromatics increased, while the levels of resins and asphaltenes decreased. Notably, the incorporation of the HPA-Ni catalyst led to significant changes in the SARA distribution: saturates increased to 29.6 wt % and aromatics to 35.6 wt %, whereas asphaltenes decreased to 16.4 wt % (Table 1). The content of saturated compounds in the oil produced through the catalytic upgrading increased more than double, while the amount of asphaltenes was cut by more than half. These observations suggest that the presence of the catalyst enhances the saturation of refractory polyaromatic compounds that make up asphaltenes and resins. This increase in saturation likely facilitates their conversion into partially saturated species that are more susceptible to cracking, primarily through ring opening mediated by the catalyst's acidic function, which agrees with the hydrocracking pathway reported in previous studies.[45,46]

3.2.4. Sulfur and Nitrogen Content. The removal of nitrogen from heavy crude oil involves hydrogenation of the nitrogen-containing rings before hydrogenolysis can occur, whereas sulfur removal follows two consecutive processes, namely, hydrogenation and direct desulfurization. Hydrodesulfurization reactions, which are irreversible, reach completion when hydrogen is supplied in the stoichiometric amount.[47,48] Using the Ni-containing heteropolyacid (HPA-Ni) catalyst resulted in a significant improvement in sulfur removal, achieving up to 31% reduction. In contrast, reactions performed without any catalyst led to only a 16.2% reduction in the sulfur content. The presence of the catalyst aids in breaking the C−S bonds of heteroatoms, as evidenced by the increased production of hydrogen sulfide (H_2S) during the catalytic process. Similarly, nitrogen removal was more effective in the presence of catalyst with a 28% reduction compared to 22% when no catalyst was used.[3,49]

The observed decrease in the amount of both total sulfur and nitrogen in the upgraded oil related to that in the heavy crude oil, give evidence that heteroatoms of sulfur and nitrogen contained in the original heavy crude oil were partially removed upon upgrading reaction.

3.2.5. Boiling Point Distribution by SIMDIS. The upgrading reaction significantly alters the molecular composition of heavy crude oil, necessitating an analysis of the changes in boiling point distribution. This was accomplished using simulated distillation analysis (SIMDIS) according to the ASTM-D2887

method.[50] Table 2 presents a comparative summary of the SIMDIS results for both the noncatalytic and catalytic routes,

Table 2. Boiling Point Distribution of Heavy Crude Oil and Upgraded Crude Oil

temperature, °C	heavy crude oil, vol %	upgraded crude oil, vol %	
		without catalyst	with HPA-Ni catalyst
TIE−221	1.35	1.75	4.88
221−343	8.83	10.5	21.04
343−540	33.53	36.6	38.16
540+	56.29	51. 15	35.92

detailing commercially important fractions such as naphtha (35−221 °C), light cyclic oil (221−343 °C), heavy cyclic oil (343−540 °C), and residue (above 540 °C). Initially, 56.3 vol % of the original heavy crude constituted the residue fraction, which decreased to 51.2 vol % without a catalyst and further reduced to 35.9 vol % with the HPA-Ni catalyst, enhancing the conversion rate of the residue from 9 to 36%.

The light fractions showed the most significant increase, particularly with catalyst usage, rising from 8.8 vol % in the untreated oil to 21.0 vol % in the upgraded oil. The quantities of naphtha and heavy oil increased modestly in the catalyzed sample compared to the untreated sample, from 1.3 to 4.9 vol % for naphtha, and from 33.5 to 38.1 vol % for heavy oil, respectively. The use of the HPA-Ni catalyst notably improved the boiling point distribution, favoring the formation of lighter hydrocarbons, including middle distillates containing diesel fuel.[51]

These findings suggest that the transformation of asphaltenes and resins occurs primarily through the direct cleavage of long side chains (dealkylation or exocyclic β-scissions) attached to aromatic and naphthenic rings, and through the ring-opening (endocyclic β-scissions) of partially hydrogenated products.[52] Other studies have reported similar transformations of asphaltenes into lighter fractions during catalytic upgrading in a methane-rich environment.[53]

3.2.6. True Boiling Point (TBP) Distribution. In refining, the quality of crude oil is often assessed based on its boiling point distribution curve. Typically, crudes with higher API gravity and greater distillate yields are rich in aromatics,[51] while those with higher sulfur content and metals tend to have lower distillate yields and API gravity.[53−56] The shift of the TBP distribution curve to the left indicates an increased level of upgrading, characterized by the conversion of high-molecular-mass compounds into lighter fractions with lower boiling points.

Using ASTM-D7169, the TBP curves for heavy crude oil and the products from the upgrading reactions, both without and with the HPA-Ni catalyst, are displayed in Figure 3. The data show that the boiling points decrease progressively from the heavy crude oil to the upgraded oil produced without a catalyst, and further decrease in the oil upgraded with the HPA-Ni catalyst. Using catalyst during the upgrading reaction promotes a shift in the TBP curve toward lighter and lower boiling species.[50] This outcome aligns with the SIMDIS analysis results of the same samples, confirming that the upgrading process involves the breakdown of heavy complex species such as asphaltenes and resins into lighter saturated and aromatic compounds, which have lower molecular mass
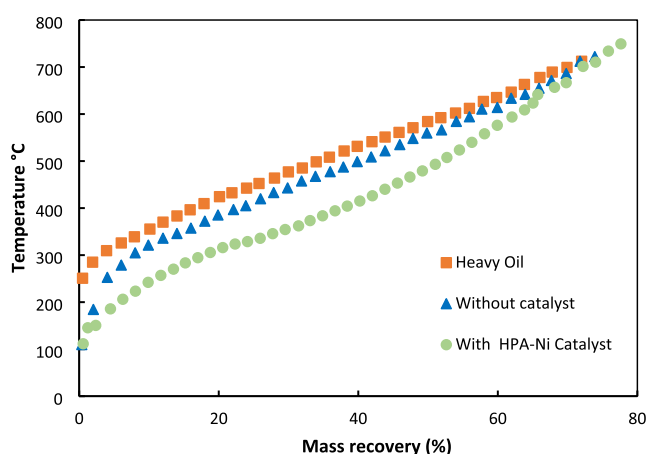

Figure 3. True boiling point (TBP) curves of heavy crude oil and upgraded oil both with and without the HPA-Ni catalyst.

and boiling points. This effect is even more pronounced with the inclusion of the HPA-Ni catalyst.

Significant shifts are observed in the temperature range of 480 to 520 °C, where the boiling point for 40% of the methane-treated oil with catalyst is notably lower compared to the untreated oil. This shift can be attributed to an increase in low boiling point fractions in the upgraded oil sample's postreaction with the catalyst. Consequently, the weight of the light cuts in the methane-treated crude oil increases to 7.53% for naphtha and kerosene, while the vacuum residue fraction decreases by 16.27%.

3.2.7. GC Analysis of Evolved Gases During the Reaction. Table 3 shows the compositions of gases produced during the

Table 3. Composition of Evolved Gaseous Products Formed During the Upgrading Reactions of Heavy Crude Oil, With and Without the Use of the HPA-Ni Catalyst

compound	natural gas, vol %	evolved gas, vol %	
		upgrading without catalyst	upgrading with HPA-Ni catalyst
CH_4	94.33	85.04	90.09
$\sum C_2$	4.01	4.52	4.44
$\sum C_3$	0.23	1.15	0.8
$\sum C_4$	0.05	0.29	0.19
C_5+	0.01	0.45	0.38
H_2	0.00	4.20	2.54
H_2S	0.00	0.42	0.13
CO_2	0.59	0.72	0.67
O_2	0.01	0.26	0.03
N_2	0.77	2.94	0.73

upgrading reactions of heavy crude oil in the presence and the absence of catalyst. Notice that the natural gas stream used in the reactions did not contain molecular hydrogen (H_2), hydrogen sulfide (H_2S), or C_2 to C_4 unsaturated hydrocarbons. However, these components were present in the gas recovered after the reactions, consistent with findings from other studies.[55,56] The formation of H_2 and H_2S indicates that hydrodesulfurization reactions occurred, which are linked to the activation of the catalyst.[50,55] Furthermore, the presence of C_2 and particularly $C_3−C_4$ hydrocarbons suggests that deep cracking of the alkyl side chains attached to asphaltenes and resins took place.
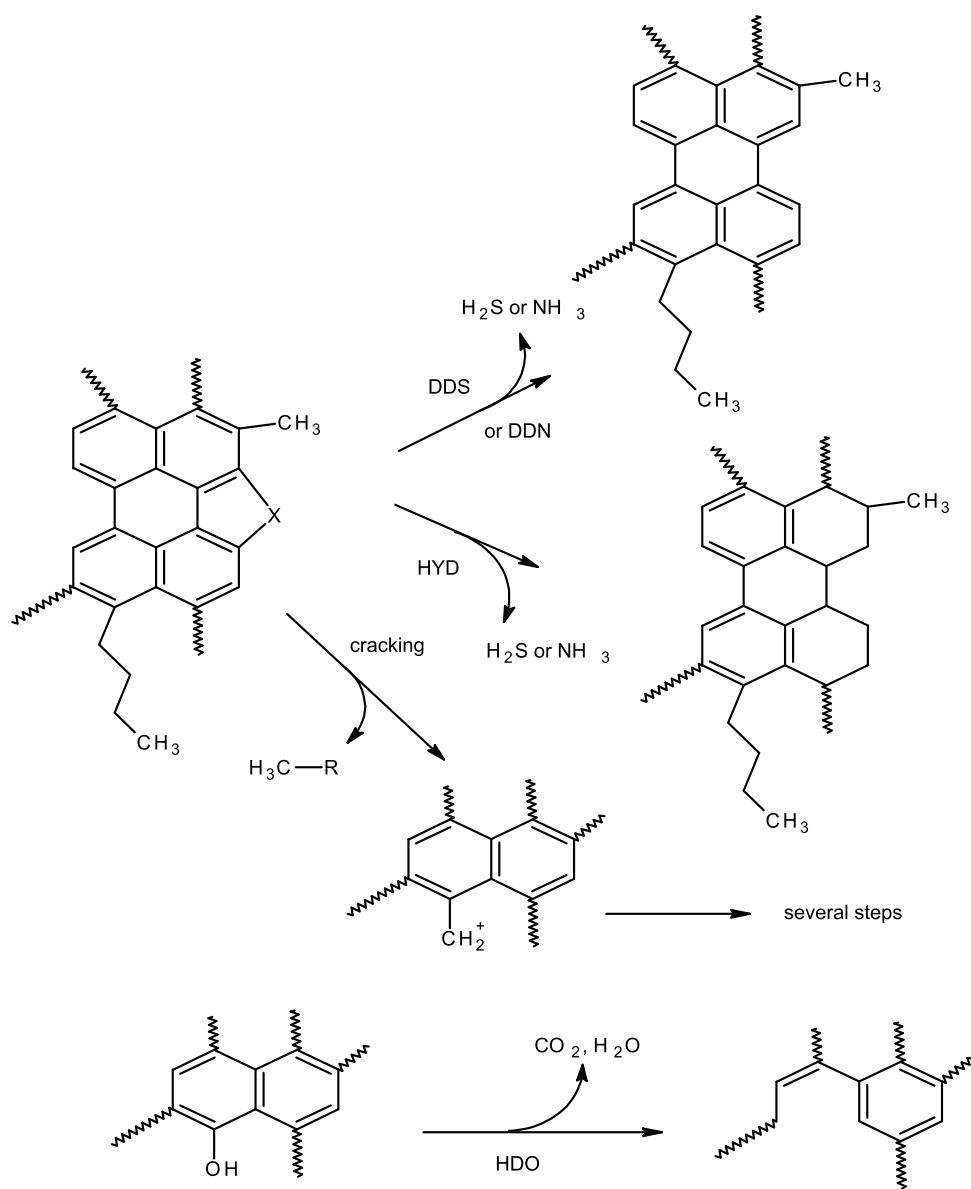
Figure 4. Hydrodesulfurization (HDT) reactions in the proposed mechanism.

Notably, the methane concentration in the recovered gas ranged from 85.1 to 90.4 mol %, values that are lower than the counterpart in the natural gas (94.3 mol %), suggesting methane consumption during the reaction. The higher methane content in the gas evolved with a catalyst compared to that without indicates methane generation via deep cracking over strong acid sites. Additionally, the recovered gas contained up to 4.2 mol % hydrogen in the absence of catalyst was used and 2.5 mol % in the presence of the HPA-Ni catalyst. This finding suggests that, in the hydrocracking pathway, a larger amount of the available hydrogen is consumed in the presence of the catalyst leading to the formation of species with a higher H/C ratio. This aligns well with the SARA distribution shown in Table 1.

3.2.8. Hypothetical Reaction Mechanism. 3.2.8.1. Hydrogen Production from Methane via HPA Catalysts. Recent studies on heteropolyacids $H_nPM1_xM2_yO_z$ (where M1 is Mo or W, and M2 is Co, Zr, Fe, or Ni) have highlighted their ability to facilitate hydrogen generation from methane, although the literature remains limited.[3,31,50,51,53−56] The nature of the reaction products from methane is influenced by the catalyst's reducibility. For instance, methane completely converts into H_2 and CO_2 over unreduced catalysts like $PW_{11}Ni$. In contrast, reduced catalysts based on Fe and Co yield hydrogen along with CH_3OH, HCHO, and CO, with only a minor production of CO_2. The C−H bond cleavage is identified as the rate-determining step, leading to the formation of CH_3 and HO radicals.[57]

3.2.8.2. Proposed Mechanism Over HPAs. In the Supporting Information, Figure S3, detailed structures of the heteropolyacids anions used in our study are given. These structures have been reproduced with permission from previous literature to illustrate the configuration of the catalytic sites.[20]

According to M.N. Timofeeva,[20] a possible structure of the title HPA is a Keggin's type with the active Mo═O supported by the characterization results described by us. The function of Mo as Mo═O in HPA-Keggin structure is activate methane as a hydrogen donor (H_3C−H) in the hydrogen formation stage followed by the formation and subsequent decomposition of

metal-oxirane, metallo-trioxolane, and molybdenum formate intermediates. Both Ni and Mo sulfides are produced for the HDT stages.

Based on cited studies, we postulate that the initial reaction involves 1,2-addition between methane (H_3C-H) and the terminal oxygen ($Mo=O$) of the HPAs.[36,58-60] This forms $HO-Mo-CH_3$ bonds, which subsequently break down into metallo-oxirane and molecular hydrogen. The oxidation of metallo-oxirane leads to the formation of metallo-trioxolane, which quickly rearranges into molybdenum formate ($HO-Mo-OC(O)H$), eventually decomposing into H_2 and CO_2, thus restoring the terminal $Mo=O$ group.

The synergy between Ni and Mo is crucial for the proper catalyst's performance. Ni facilitates hydrogenation reactions, while Mo in the Keggin structure aids in methane activation and the formation of reactive intermediates. This comprehensive interaction enhances the catalyst's efficiency in upgrading heavy crude oil.

3.2.8.3. Hydrotreating and Hydrocracking Processes. In the typical hydrotreating process, the disappearance of thiophene-type compounds correlates well with an increase in the number of aromatic rings (Figure 4). Nonthiophene aromatic sulfur compounds react more rapidly than dibenzothiophenes, reflecting the challenges in substituting dibenzothiophene rings with alkyl groups. The overall hydrodesulfurization (HDS) reaction can proceed via two main pathways (i) hydrogenolysis replacing C−S bonds with C−H bonds open to ring opening, and (ii) hydrogenation, which initially saturates aromatic rings before undergoing hydrogenolysis.[56] The hydrodenitrogenation (HDN) reaction involves the cleavage of the C (sp3) bond.[61] Hydrocracking typically occurs via the formation of intermediate carbenium ions, facilitated by the acidic sites on the catalyst thereby promoting hydrogenation-dehydrogenation reactions. The hydrodeoxygenation (HDO) process presumably produces oxygenated byproducts such as H_2O and CO_2 in the gas fraction.[62] The HDO reaction, in turn, presumably occurs with oxygenated byproducts in the gas fraction, H_2O and CO_2.

The results from the reaction indicate that breakdown of complex hydrocarbons occurred, as evidenced by an increase in saturated and aromatic compounds in the products, while the level of asphaltenes and resins decreased. This transformation typically results from hydrocracking and hydrotreating reactions, both of which utilize the same active metal phases to cleave hydrocarbons chains. Consequently, the breakdown of nitrogen and sulfur heteroatoms can also be anticipated during these processes.[63]

4. CONCLUSIONS

The results presented in this manuscript clearly demonstrate that the use of a catalyst composed of heteropolyacid (HPA) modified with nickel, combined with a methane-rich natural gas stream, significantly improves the quality of heavy crude oil with an initial 8.0°API (at 15.5 °C). This was achieved through an upgrading liquid phase homogeneous reaction. Notably, methane served as an effective hydrogen donor, which facilitates the partial hydrogenation of polyaromatic species - an essential step preceding the cracking reactions on the catalyst's acidic sites.

A proposed mechanism for hydrogen production involves a 1,2-addition reaction between methane (H_3C-H) and the terminal oxygen ($Mo=O$) of the Keggin-structured HPA, followed by the formation and subsequent decomposition of

metal-oxirane, metallo-trioxolane, and molybdenum formate intermediates. The gas chromatography analysis of gases evolved during the upgrading confirmed the formation of molecular hydrogen and the consumption of methane.

The upgrading process, conducted in a batch system at 380 °C and 4.4 MPa for 2 h to mimic reservoir conditions, resulted in a notable increase in API gravity (from 8.0 to 16°API at 37.5 °C) and a significant reduction in kinematic viscosity (from 2200 to 125 cSt at 37.5 °C). Additionally, the content of asphaltenes decreased from 38.7 to 16.4 wt %, sulfur content reduced from 5.9 to 4.0 wt %, and nitrogen levels dropped from 971 to 695 ppm. Moreover, there was a substantial increase in the volume of light distillates (from 1.3 to 4.9 vol %) and particularly in middle distillates (from 8.8 to 21.0 vol %). These findings underscore the potential of using nickel-modified HPA catalysts, in conjunction with methane as a hydrogen donor, as an effective strategy for upgrading heavy crude oil.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c04801.

> Methods of characterization of the catalyst; methods of characterization of heavy crude oil and reaction products; neutralization profile of the HPA-Ni catalyst (Figure S1); FTIR spectra of the HPA-Ni catalyst (Figure S2); the structures of heteropolyanions. Copyright Elsevier B.V. (Figure S3) (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Alma Delia Miranda-Olvera − *Instituto Mexicano del Petróleo, Ciudad de México 07730, México;* ⓞ orcid.org/0000-0001-6356-6392; Email: admiranda@imp.mx

Authors

Persi Schacht-Hernández − *Instituto Mexicano del Petróleo, Ciudad de México 07730, México*

Federico Jiménez-Cruz − *Instituto Mexicano del Petróleo, Ciudad de México 07730, México*

Oscar Morelos-Santos − *Tecnológico Nacional de México/Instituto Tecnológico de Ciudad Madero, Ciudad Madero, Tamaulipas 89440, México*

José Luis García-Gutiérrez − *Instituto Mexicano del Petróleo, Ciudad de México 07730, México;* ⓞ orcid.org/0000-0002-1181-876X

Roberto Quintana-Solórzano − *Instituto Mexicano del Petróleo, Ciudad de México 07730, México;* ⓞ orcid.org/0000-0001-6949-2291

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.4c04801

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Uchenna Babalola, F.; Akpoveta Susu, A. Pre-Treatment of Heavy Crude Oils for Refining. In *Processing of Heavy Crude Oils - Challenges and Opportunities*; IntechOpen, 2019 DOI: 10.5772/intechopen.89486.

(2) Jing, J.; Yin, R.; Yuan, Y.; Shi, Y.; Sun, J.; Zhang, M. Determination of the Transportation Limits of Heavy Crude Oil Using Three Combined Methods of Heating, Water Blending, and Dilution. *ACS Omega* 2020, 5 (17), 9870−9884.

(3) Zhao, F.; Liu, Y.; Lu, N.; Xu, T.; Zhu, G.; Wang, K. A Review on Upgrading and Viscosity Reduction of Heavy Oil and Bitumen by Underground Catalytic Cracking. *Energy Rep.* 2021, 7, 4249−4272.

(4) https://www.eia.gov/outlooks/aeo/IIF_carbonfee/. (accessed Feb 26, 2024).

(5) Hamedi Shokrlu, Y.; Babadagli, T. In-Situ Upgrading of Heavy Oil/Bitumen During Steam Injection by Use of Metal Nanoparticles: A Study on In-Situ Catalysis and Catalyst Transportation. *SPE Reservoir Eval. Eng.* 2013, 16 (03), 333−344.

(6) Santos, R. G.; Loh, W.; Bannwart, A. C.; Trevisan, O. V. An Overview of Heavy Oil Properties and Its Recovery and Transportation Methods. *Braz. J. Chem. Eng.* 2014, 31 (3), 571−590.

(7) Omar, S.; Yang, Y.; Wang, J. A Review on Catalytic & Non-Catalytic Bio-Oil Upgrading in Supercritical Fluids. *Front. Chem. Sci. Eng.* 2021, 15 (1), 4−17.

(8) Schachtl, E.; Kondratieva, E.; Gutiérrez, O. Y.; Lercher, J. A. Pathways for H_2 Activation on (Ni)-MoS$_2$ Catalysts. *J. Phys. Chem. Lett.* 2015, 6 (15), 2929−2932.

(9) Alemán-Vázquez, L. O.; Torres-Mancera, P.; Ancheyta, J.; Ramírez-Salgado, J. Use of Hydrogen Donors for Partial Upgrading of Heavy Petroleum. *Energy Fuels* 2016, 30 (11), 9050−9060.

(10) Johnstone, R. A. W.; Wilby, A. H.; Entwistle, I. D. Heterogeneous Catalytic Transfer Hydrogenation and Its Relation to Other Methods for Reduction of Organic Compounds. *Chem. Rev.* 1985, 85 (2), 129−170.

(11) Ovalles, C.; Hamana, A.; Rojas, I.; Bolívar, R. A. Upgrading of Extra-Heavy Crude Oil by Direct Use of Methane in the Presence of Water. *Fuel* 1995, 74 (8), 1162−1168.

(12) He, P.; Song, H. Catalytic Natural Gas Utilization on Unconventional Oil Upgrading. In *Advances in Natural Gas Emerging Technologies*; InTech, 2017 DOI: 10.5772/66640.

(13) Guo, A.; Wu, C.; He, P.; Luan, Y.; Zhao, L.; Shan, W.; Cheng, W.; Song, H. Low-Temperature and Low-Pressure Non-Oxidative Activation of Methane for Upgrading Heavy Oil. *Catal. Sci. Technol.* 2016, 6 (4), 1201−1213.

(14) Sánchez-Bastardo, N.; Schlögl, R.; Ruland, H. Methane Pyrolysis for Zero-Emission Hydrogen Production: A Potential Bridge Technology from Fossil Fuels to a Renewable and Sustainable Hydrogen Economy. *Ind. Eng. Chem. Res.* 2021, 60 (32), 11855−11881.

(15) Speight, J. G. Waste Gasification for Synthetic Liquid Fuel Production. In *Gasification for Synthetic Fuel Production*; Elsevier, 2015; pp 277−301 DOI: 10.1016/B978-0-85709-802-3.00012-6.

(16) Yoshimura, Y.; Yoshitomi, S.; Ooishi, K.; Sato, T.; Shimada, H.; Matsubayashi, N.; Nishijima, A. Ruthenium Promoted Nickel-Molybdate Catalysts for Hydrotreating Coal-Derived Oils. In *1991 International Conference on Coal Science Proceedings*; Elsevier, 1991; pp 818−821 DOI: 10.1016/B978-0-7506-0387-4.50207-2.

(17) Kozhevnikov, I. V. Sustainable Heterogeneous Acid Catalysis by Heteropoly Acids. *J. Mol. Catal. A Chem.* 2007, 262 (1−2), 86−92.

(18) Ovalles, C.; Filgueiras, E.; Morales, A.; Rojas, I.; de Jesus, J. C.; Berrios, I. Use of a Dispersed Molybdenum Catalyst and Mechanistic Studies for Upgrading Extra-Heavy Crude Oil Using Methane as Source of Hydrogen. *Energy Fuels* 1998, 12 (2), 379−385.

(19) Shi, W.; Zhao, J.; Yuan, X.; Wang, S.; Wang, X.; Huo, M. Effects of Brønsted and Lewis Acidities on Catalytic Activity of Heteropolyacids in Transesterification and Esterification Reactions. *Chem. Eng. Technol.* 2012, 35 (2), 347−352.

(20) Timofeeva, M. N. Acid Catalysis by Heteropoly Acids. *Appl. Catal. A Gen* 2003, 256 (1−2), 19−35.

(21) Yang, G.; Dilixiati, D.; Yang, T.; Liu, D.; Yu, B.; Hu, C. Phosphomolybdic Acid as a Bifunctional Catalyst for Friedel−Crafts Type Dehydrative Coupling Reaction. *Appl. Organomet. Chem.* 2018, 32 (9), No. e4450, DOI: 10.1002/aoc.4450.

(22) Yu, M.-a.; Feng, Y.; Gao, L.; Lin, S. Phosphomolybdic Acid Supported Single-Metal-Atom Catalysis in CO Oxidation: First-Principles Calculations. *Phys. Chem. Chem. Phys.* 2018, 20 (31), 20661−20668.

(23) Ovalles, C.; Rivero, V.; Salazar, A. Downhole Upgrading of Orinoco Basin Extra-Heavy Crude Oil Using Hydrogen Donors under Steam Injection Conditions. Effect of the Presence of Iron Nanocatalysts. *Catalysts* 2015, 5 (1), 286−297.

(24) Ramos, M.; Galindo-Hernández, F.; Torres, B.; Domínguez-Esquivel, J. M.; Heilmaier, M. In Situ Thermal-Stage Fitted-STEM Characterization of Spherical-Shaped Co/MoS2 Nanoparticles for Conversion of Heavy Crude Oils. *Catalysts* 2020, 10 (11), 1239.

(25) Saraev, A. A.; Zaikina, O. O.; Sosnin, G. A.; Yeletsky, P. M.; Tsapina, A. M.; Zubavichus, Y. V.; Yakovlev, V. A.; Kaichev, V. V. XAS Study of Mo-Based Dispersed Catalysts for Upgrading of Heavy Oil. *Radiat. Phys. Chem.* 2020, 175, No. 108335.

(26) Safaei Mahmoudabadi, Z.; Rashidi, A.; Panahi, M. New Approach to Unsupported ReS2 Nanorod Catalyst for Upgrading of Heavy Crude Oil Using Methane as Hydrogen Source. *Int. J. Hydrogen Energy* 2021, 46 (7), 5270−5285.

(27) Urazov, K. Kh.; Sviridenko, N. N.; Iovik, Y. A.; Kolobova, E. N.; Grabchenko, M. V.; Kurzina, I. A.; Mukhamatdinov, I. I. Effect of Hydrogen-Donor of Heavy Crude Oil Catalytic Aquathermolysis in the Presence of a Nickel-Based Catalyst. *Catalysts* 2022, 12 (10), 1154.

(28) Al-Muntaser, A. A.; Varfolomeev, M. A.; Suwaid, M. A.; Saleh, M. M.; Djimasbe, R.; Yuan, C.; Zairov, R. R.; Ancheyta, J. Effect of Decalin as Hydrogen-Donor for in-Situ Upgrading of Heavy Crude Oil in Presence of Nickel-Based Catalyst. *Fuel* 2022, 313, No. 122652.

(29) Khamieva, A. N.; Al-Muntaser, A. A.; Suwaid, M. A.; Djimasbe, R.; Reyimkulyyeva, S. U.; Emelianov, D. A.; Varfolomeev, M. A. Synthesis and Application of a Ni-Based Dispersed Catalyst for Hydrothermal Upgrading of Heavy Crude Oil. *Energy Fuels* 2024, 38 (2), 1204−1215.

(30) Cid, R.; Pecchi, G. Potentiometric Method for Determining the Number and Relative Strength of Acid Sites in Colored Catalysts. *Appl. Catal* 1985, 14, 15−21.

(31) Rocchiccioli-Deltcheff, C.; Aouissi, A.; M Bettahar, M.; Launay, S.; Fournier, M. Catalysis by 12-Molybdophosphates. *J. Catal.* 1996, 164 (1), 16−27.

(32) Mandal, K. C.; Ozanam, F.; Chazalviel, J.-N. In-Situ Infrared Investigations of the Electrochemistry of Heteropolyacids at n-Ge Electrodes. *J. Electroanal. Chem.* 1992, 336 (1−2), 153−170.

(33) Karthikeyan, R.; Thangaraju, D.; Prakash, N.; Hayakawa, Y. Single-Step Synthesis and Catalytic Activity of Structure-Controlled Nickel Sulfide Nanoparticles. *CrystEngComm* 2015, 17 (29), 5431−5439.

(34) Mazari, T.; Marchal, C. Roch.; Hocine, S.; Salhi, N.; Rabia, C. Oxidation of Propane over Ammonium-Transition Metal Mixed Keggin Phosphomolybdate Salts. *J. Nat. Gas Chem.* 2010, 19 (1), 54−60.

(35) Zhou, X.; Mandia, D. J.; Park, H.; Balasubramanian, M.; Yu, L.; Wen, J.; Yakovenko, A.; Chung, D. Y.; Kanatzidis, M. G. New Compounds and Phase Selection of Nickel Sulfides via Oxidation State Control in Molten Hydroxides. *J. Am. Chem. Soc.* 2021, 143 (34), 13646−13654.

(36) Hadad, C. M.; Paul, R. R.; Kenneth, B. W. C−O and C−S Bonds: Stability, Bond Dissociation Energies, and Resonance Stabilization. *J. Org. Chem.* 1998, 63 (24), 8668−8681.

(37) Sasca, V.; Ştefănescu, M.; Popa, A. Studies on the Non-Isothermal Decomposition of H3PMo12O40 Center Dot XH(2)O and H4PVMo11O40 Center Dot YH(2)O. *J. Therm. Anal. Calorim.* 1999, 56 (2), 569−578.

(38) Al-zaqri, N.; Alsalme, A.; Adil, S. F.; Alsaleh, A.; Alshammari, S. G.; Alresayes, S. I.; Alotaibi, R.; Al-Kinany, M.; Siddiqui, M. R. H.

Comparative Catalytic Evaluation of Nickel and Cobalt Substituted Phosphomolybdic Acid Catalyst Supported on Silica for Hydrodesulfurization of Thiophene. *J. Saudi Chem. Soc.* **2017**, *21* (8), 965−973.

(39) Micek-Ilnicka, A. The Role of Water in the Catalysis on Solid Heteropolyacids. *J. Mol. Catal. A Chem.* **2009**, *308* (1−2), 1−14.

(40) Jing, F.; Katryniok, B.; Bordes-Richard, E.; Dumeignil, F.; Paul, S. Structural Evolution under Reaction Conditions of Supported (NH4)3HPMo11VO40 Catalysts for the Selective Oxidation of Isobutane. *Catalysts* **2015**, *5* (1), 460−477.

(41) Ishikawa, S.; Ikeda, T.; Koutani, M.; Yasumura, S.; Amakawa, K.; Shimoda, K.; Jing, Y.; Toyao, T.; Sadakane, M.; Shimizu, K.; Ueda, W. Oxidation Catalysis over Solid-State Keggin-Type Phosphomolybdic Acid with Oxygen Defects. *J. Am. Chem. Soc.* **2022**, *144* (17), 7693−7708.

(42) Barth, T.; Moen, L.; Dyrkorn, C.Comparison of Acid Numbers and Carboxylic Acid Molecular Compositions in Biodegraded and Normal Crude Oils. *Preprints-American Chemical Society Division of Petroleum Chemistry* 1998; Vol. *43*, pp 134−136.

(43) Zhang, Q.; Luo, Q.; Wu, Y.; Yu, R.; Cheng, J.; Zhang, Y. Construction of a Keggin Heteropolyacid/Ni-MOF Catalyst for Esterification of Fatty Acids. *RSC Adv.* **2021**, *11* (53), 33416−33424.

(44) Li, Z.; Li, Y.; Xu, H.; Jarvis, J.; Meng, S.; Song, H. Effect of Methane Presence on Catalytic Heavy Oil Partial Upgrading. *Fuel* **2021**, *297*, No. 120733.

(45) Barth, T.; Høiland, S.; Fotland, P.; Askvik, K. M.; Myklebust, R.; Erstad, K. Relationship between the Content of Asphaltenes and Bases in Some Crude Oils. *Energy Fuels* **2005**, *19* (4), 1624−1630.

(46) Shabib-Asl, A.; Ayoub, M. A.; Elraies, K. A. A New Hybrid Technique Using Low Salinity Water Injection and Foam Flooding for Enhanced Oil Recovery in Sandstone Rock. *J. Pet. Sci. Eng.* **2019**, *174*, 716−728.

(47) Sánchez-Minero, F.; Sánchez-Reyna, G.; Ancheyta, J.; Marroquin, G. Comparison of Correlations Based on API Gravity for Predicting Viscosity of Crude Oils. *Fuel* **2014**, *138*, 193−199.

(48) RezaeiDoust, A.; Puntervold, T.; Austad, T. Chemical Verification of the EOR Mechanism by Using Low Saline/Smart Water in Sandstone. *Energy Fuels* **2011**, *25* (5), 2151−2162.

(49) He, P.; Luan, Y.; Zhao, L.; Cheng, W.; Wu, C.; Chen, S.; Song, H. Catalytic Bitumen Partial Upgrading over Ag-Ga/ZSM-5 under Methane Environment. *Fuel Process. Technol.* **2017**, *156*, 290−297.

(50) Santos, J. M.; Vetere, A.; Wisniewski, A.; Eberlin, M.; Schrader, W. Comparing Crude Oils with Different API Gravities on a Molecular Level Using Mass Spectrometric Analysis. Part 2: Resins and Asphaltenes. *Energies* **2018**, *11* (10), 2767.

(51) Alonso-Ramírez, G.; Cuevas-García, R.; Sanchez-Minero, F.; Ramírez, J.; Moreno-Montiel, M.; Ancheyta, J.; Carbajal-Vielman, R. Catalytic Hydrocracking of a Mexican Heavy Oil on a MoS2/Al2O3 Catalyst: I. Study of the Transformation of Isolated Saturates Fraction Obtained from SARA Analysis. *Catal. Today* **2020**, *353*, 153−162.

(52) Ruiz-Morales, Y.; Miranda-Olvera, A. D.; Portales-Martínez, B.; Domínguez, J. M. Experimental and Theoretical Approach To Determine the Average Asphaltene Structure of a Crude Oil from the Golden Lane (Faja de Oro) of Mexico. *Energy Fuels* **2020**, *34* (7), 7985−8006.

(53) Roussis, S. G.; Fitzgerald, W. P. Gas Chromatographic Simulated Distillation-Mass Spectrometry for the Determination of the Boiling Point Distributions of Crude Oils. *Anal. Chem.* **2000**, *72* (7), 1400−1409.

(54) Schacht-Hernández, P.; Portales-Martínez, B.; Laredo, G. C.; Pérez-Romo, P.; Domínguez-Esquivel, J. M. Homogeneous Catalyst for In-Situ Hydrotreating of Heavy Oils. *Appl. Catal., A* **2019**, *577*, 99−106.

(55) Prado, G. H. C.; Rao, Y.; de Klerk, A. Nitrogen Removal from Oil: A Review. *Energy Fuels* **2017**, *31* (1), 14−36.

(56) Hart, A.; Wood, J.; Greaves, M. In Situ Catalytic Upgrading of Heavy Oil Using a Pelletized Ni-Mo/Al2O3 Catalyst in the THAI Process. *J. Pet. Sci. Eng.* **2017**, *156*, 958−965.

(57) Ni, J.; Zhao, J.; Chen, L.; Lin, J.; Kawi, S. Lewis Acid Sites Stabilized Nickel Catalysts for Dry (CO_2) Reforming of Methane. *ChemCatChem* **2016**, *8* (24), 3732−3739.

(58) Maestre, J. M.; Lopez, X.; Bo, C.; Poblet, J.-M.; Casañ-Pastor, N. Electronic and Magnetic Properties of α-Keggin Anions: A DFT Study of $[XM_{12}O_{40}]^{n-}$, (M = W, Mo; X = Al III, Si IV, P V, Fe III, Co II, Co III) and $[SiM_{11}VO_{40}]^{m-}$ (M = Mo and W). *J. Am. Chem. Soc.* **2001**, *123* (16), 3749−3758.

(59) Yi, Y.; Li, S.; Ding, F.; Yu, H. Change of Asphaltene and Resin Properties after Catalytic Aquathermolysis. *Pet Sci.* **2009**, *6* (2), 194−200.

(60) Kadhim, A. Correlation between Trace Metals of Crude Oils with Sulfur and API in Maysan Province Southern Iraq *Int. J. Manage. Sci. Technol.* 2015; Vol. 3 3.

(61) Al-Muntaser, A. A.; Varfolomeev, M. A.; Suwaid, M. A.; Feoktistov, D. A.; Yuan, C.; Klimovitskii, A. E.; Gareev, B. I.; Djimasbe, R.; Nurgaliev, D. K.; Kudryashov, S. I.; Egorova, E. V.; Fomkin, A. V.; Petrashov, O. V.; Afanasiev, I. S.; Fedorchenko, G. D. Hydrogen Donating Capacity of Water in Catalytic and Non-Catalytic Aquathermolysis of Extra-Heavy Oil: Deuterium Tracing Study. *Fuel* **2021**, *283*, No. 118957.

(62) Maity, S. K.; Ancheyta, J.; Marroquín, G. Catalytic Aquathermolysis Used for Viscosity Reduction of Heavy Crude Oils: A Review. *Energy Fuels* **2010**, *24* (5), 2809−2816.

(63) Correa, A.; León, T.; Martin, R. Ni-Catalyzed Carboxylation of $C(Sp^2)−$ and $C(Sp^3)−O$ Bonds with CO_2. *J. Am. Chem. Soc.* **2014**, *136* (3), 1062−1069.