






## Article

# Octahedral Cluster Complex of Molybdenum as Oil-Soluble Catalyst for Improving In Situ Upgrading of Heavy Crude Oil: Synthesis and Application

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**Abstract:** Heavy oil resources are attracting considerable interest in terms of sustaining energy demand. However, the exploitation of such resources requires deeper understanding of the processes occurring during their development. Promising methods currently used for enhancing heavy oil recovery are steam injection methods, which are based on aquathermolysis of heavy oil at higher temperatures. Regardless of its efficiency in the field of in situ upgrading of heavy oil, this technique still suffers from energy consumption and inefficient heat transfer for deeper reservoirs. During this study, we have developed a molybdenum-based catalyst for improving the process of heavy oil upgrading at higher temperature in the presence of water. The obtained catalyst has been characterized by a set of physico-chemical methods and was then applied for heavy oil hydrothermal processing in a high-pressure reactor at 200, 250 and 300 °C. The comparative study between heavy oil hydrothermal upgrading in the presence and absence of the obtained molybdenum-based oil soluble catalysts has pointed toward its potential application for heavy oil in situ upgrading techniques. In other words, the used catalyst was able to reduce heavy oil viscosity by more than 63% at 300 °C. Moreover, our results have demonstrated the efficiency of a molybdenum-based catalyst in improving saturates and light hydrocarbon content in the upgraded oil compared to the same quantity of these fractions in the initial oil and in the non-catalytically upgraded oil at similar temperatures. This has been explained by the significant role played by the used catalyst in destructing asphaltenes and resins as shown by XRD, elemental analysis, and gas chromatography, which confirmed the presence of molybdenum sulfur particles in the reaction medium at higher temperatures, especially at 300 °C. These particles contributed to stimulating hydrodesulphurization, cracking and hydrogenation reactions by breaking down the C-heteroatom bonds and consequently by destructing asphaltenes and resins into smaller fractions, leading to higher mobility and quality of the upgraded oil. Our results add to the growing body of literature on the catalytic upgrading of heavy oil in the presence of transition metal particles.

**Keywords:** heavy crude oil; evaluating upgraded oil; catalytic aquathermolysis; non-catalytic upgrading; oil-soluble catalyst; in situ catalytic upgrading; enhanced oil recovery

## 1. Introduction

It is common knowledge that industrial development and rapid population growth are the main causes of energy demand rises, which are expected to witness a considerable growth by more than 34% with an annual rate of 1.6% on average [1]. Furthermore, the

decline in conventional oil reserves such as light oil and natural gas, which represent approximately 30% of the world's oil resources and are considered the most consumed in the petrochemical industry, would require finding other resources that could sustain the development of modern society [2]. In the literature, unconventional oil often refers to heavy oil, extra-heavy oil, and bitumen, which will account for 80% of all energy until 2035 [3]. The fundamental characteristics of unconventional oil are high viscosity and density, which are associated with the large amount of asphaltenes, resins, and heavy metals such as nickel and vanadium, which consequently complicate their extraction [4–6].

Various methods and techniques known as enhanced oil recovery (EOR) have been proposed and implemented for the extraction of heavy and extra-heavy oils. In the classical approach, EOR methods are classified into chemical, physical and thermal methods. The chemical EOR methods are based on the injection of chemicals into the reservoir to weaken the water/oil interface and to facilitate the production of heavy oil by increasing its mobility in situ. However, the physical EOR methods are based on increasing oil temperature in situ by applying physical sources of energy such as electromagnetic heating or microwave field applications. Thermal EOR are based on generating heat within the reservoir to decrease heavy oil viscosity in situ such as steam injection or in situ combustion techniques. In recent years, there has been growing interest in steam injection because of its efficiency and economic advantage compared to other methods.

Much work has been carried out on the potential of steam injection in improving and facilitating heavy oil recovery by increasing reservoir temperature (around 300–350 °C) and decreasing oil viscosity in situ, yet there are still some critical issues regarding reversible viscosity of the produced oil that complicate its transportation and refining processes [7]. Many works have proposed the use of catalysts in order to solve this issue [7–9]. It is common knowledge that the applied catalysts in the field of EOR are categorized into oil-soluble, water-soluble and nanoparticle catalysts.

A growing body of literature has examined the effect of nanoparticles and water-soluble catalysts on enhancing heavy oil recovery by steam injection. Sitnov et al. [10] have studied the effects of iron oxide nanoparticles on the process of aquathermolysis. The obtained data indicated that iron oxide nanoparticles can destruct asphaltene and resin molecules through the cleavage of C-heteroatoms bonds. Another work [11] has reviewed the effect of water-soluble catalysts on aquathermolysis of heavy oil. It has been reported that water-soluble catalysts improve the viscosity and average molecular weight of the produced oil after aquathermolysis.

Regardless of the effect generated by the application of nanoparticles and water-soluble catalysts, their effect on the process of heavy oil recovery via steam injection in real conditions is still, unfortunately, far away from successful application due to the non-mixing of oil with these compounds. In other words, the major drawback to adopting nanoparticles is the high degree of their aggregation during the process of heavy oil aquathermolysis, which occurs at higher temperatures [12]. Moreover, it is common knowledge that water-soluble catalysts have poor dispersion in oil, which reduces their efficiency due to the lack of catalytic surface contact with heavy oil components.

An alternative solution that is slightly less complicated and more effective in terms of solubility, dispersion and high contact with heavy oil's compounds is presented by the application of oil-soluble catalysts on the basis of different transition metals. In their work, Khelkhal et al. [13] have studied the impact generated from the use of iron-based oil soluble catalysts on the performance of heavy oil pyrolysis and aquathermolysis. The obtained data have shown a positive effect of iron tallates on decreasing the activation energy of the pyrolysis processes. Moreover, it has been found that iron tallates contribute to decreasing the amount of asphaltenes and resins with an increase in saturated hydrocarbons in the produced oil [9,14]. Furthermore, it has been found [15] that the high content of hydrogen-containing feedstocks in oil-soluble catalysts allows them to engage in a variety of reactions other than cracking, such as hydrogenation and hydrodesulfurization. In addition, the small amount of metal in the oil-soluble catalysts (5–15%) makes their use cost-effective [16].

Many studies have been conducted on the performance and role of molybdenum-supported precursors in heavy oil upgrading [17,18]. Some of them have focused on the reaction mechanism during heavy oil upgrading in the presence of catalysts [19], including molybdenum-based catalysts. To date, quite a wide variety of oil-soluble precursors have been reported, most of which are organometallic complexes with hydrophobic bonds such as carbonyls [20], naphthenates [21], acetylacetonate [22], and calixarenes [23]. Because of the formation of MoS<sub>2</sub> with a unique layered structure, oil-soluble Mo precursors are among the most effective in terms of coke suppression, hydrogenation, and hydrodesulphurization. The terminal sites of MoS<sub>2</sub> catalyze hydrodesulphurization, while the edge sites catalyze hydrodesulfurization and hydrogenation, according to the rim-edge model [24]. It was found that decreasing the particle size of MoS<sub>2</sub> and the number of stacked layers increases the number of edges and edge-active sites. Based on this result, reduced particle sizes of MoS<sub>2</sub> can be achieved by controlling the uniformity of the oil-soluble Mo precursor's nucleation process, the dispersion function, thermal decomposition behavior, and thus the Mo precursor's molecular design. New organic molybdenum compounds, such as Mo-triphenylphosphines [25] and Mo-aminomethylphosphonates [26], are currently being investigated for hydrocracking applications.

Saraev et al. [27] studied the effect of various commercial and non-commercial (MoCoP/Al<sub>2</sub>O<sub>3</sub> and MoWNiCo/Al<sub>2</sub>O<sub>3</sub>) catalysts on heavy crude oil hydrothermal processing in a bench reactor for 4 h at 350 °C under 1566 psi. The obtained results have shown an increase in heavy oil API gravity from 12.5 to 21–26 API, a decrease in the kinematic viscosity from 18,130 to 8–100 cSt at 298 K, and a reduction in asphaltene content from 26 to 7 wt%. The obtained data showed sulfur removal as well by 30% to 60%, and an increase in the amount of light hydrocarbons from 20% to 30%. In their work, Rashid S. Al-Hajri et al. [28] have investigated Omani heavy oil upgrading by means of aquathermolysis in the presence of NiMo and CoMo mixing as bimetallic catalysts. The obtained data showed a viscosity reduction of up to 95% with a catalyst concentration of 2%, a water concentration of 5%, and a reaction temperature of 300 °C, in addition to cracking long carbon chains and converting them to shorter carbon chains. The binary catalysts also reduced sulfur and improved the quality of Omani heavy oil.

Mo-based oil-soluble catalyst supported by [Mo<sub>6</sub>X<sub>8</sub>L<sub>6</sub>]<sup>n-</sup> (where X, L = Cl-, Br-, or I-), referred to as octahedral halogen Mo clusters (Mo OHCs), are known to have excellent performances in extensive applications, such as electrocatalysis, hydrogenation, and desulfurization processes. To date, Mo OHCs have never been examined in heavy and extra-heavy oil upgrading. In the present study, the catalytic performance of (DDA)<sub>2</sub>[(Mo<sub>6</sub>Br<sub>8</sub>)Br<sub>6</sub>] (where DDA is N,N-dimethyl-N-octadecyloctadecan-1-amonium, C<sub>38</sub>H<sub>80</sub>N<sup>+</sup>) as a precursor for forming MoS<sub>2</sub> nanoparticles in heavy oil upgrading was thoroughly investigated by means of different physical and chemical analyses.

## 2. Experimental

### 2.1. Materials

To perform our study, we used a sample of heavy oil obtained from the Ashalcha field in the republic of Tatarstan, Russia. The physical properties of the opted sample are presented in Table 1.

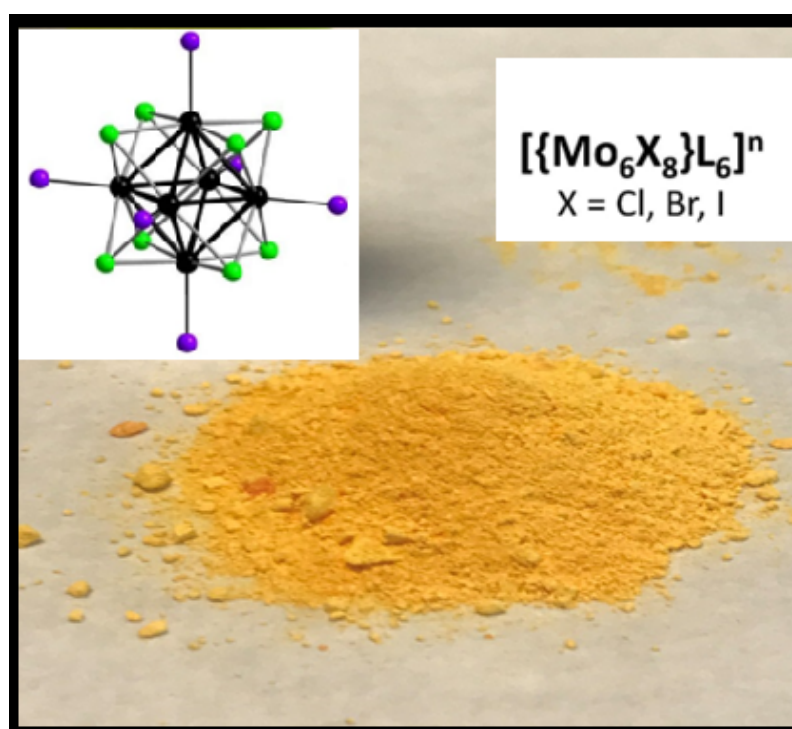
### 2.2. Catalyst Synthesis

The obtained powder of molybdenum octahedral cluster complex [DDA<sub>2</sub>(Mo<sub>6</sub>Br<sub>8</sub>)Br<sub>6</sub>] constituted of two parts: the first one is composed of N,N-dimethyl-N-octadecyloctadecan-1-amonium, C<sub>38</sub>H<sub>80</sub>N<sup>+</sup>, referred to as DDA<sub>2</sub> throughout the text. The second part is a complex of (Mo<sub>6</sub>Br<sub>8</sub>)Br<sub>6</sub>. The most striking property of the obtained catalysts is the ability to disperse within the oil volume because of interactions with long-chain aliphatic parts of the oil's molecules (Figure 1). Cluster Cs<sub>2</sub>[(Mo<sub>6</sub>Br<sub>8</sub>)Br<sub>6</sub>] was obtained according to a well-known procedure [29]. C<sub>38</sub>H<sub>80</sub>NCl (1.2 g, 2.1 mmol) was dissolved in 7 mL of ethanol and was added to the solution of Cs<sub>2</sub>[(Mo<sub>6</sub>Br<sub>8</sub>)Br<sub>6</sub>] (1.5 g, 0.8 mmol) in acetone (200 mL).

The mixture was stirred for 5 h at 60 °C and 12 h at room temperature. Then, the solution was filtered and evaporated to dryness. Obtained orange powder was washed twice with hot water, dissolved in acetone, and filtered. Solution was evaporated, and oily residue was obtained. To obtain a fine powder, the substance was washed with 50 mL of ethanol. Obtained  $(\text{DDA})_2[\{\text{Mo}_6\text{Br}_8\}\text{Br}_6]$  was separated and dried at room temperature. Yield is 1.6 g (70%). For  $\text{C}_{76}\text{H}_{160}\text{N}_2\text{Mo}_6\text{Br}_{14}$  calculated (%): C 32.6, H 5.8, N 1.0; found (%): C 32.9, H 5.8, N 1.1. EDX: Mo:Br ratio of 6:14.4.  $^1\text{H-NMR}$  in  $d_6\text{-DMSO}$ : 3.25–3.18 (4H), 3.00–2.94 (6H), 1.67–1.58 (4H), 1.35–1.20 (60H), 0.88–0.83 (6H). The synthesis procedure was performed via two stages: Firstly,  $\text{Cs}_2[\text{Mo}_6\text{Br}_8\text{Br}_6]$  was obtained by combining high-temperature ampoules of Mo, Cs Br, and  $\text{Br}_2$ . Then,  $\text{Cs}_2[\{\text{Mo}_6\text{Br}_8\}\text{Br}_6]$  was created by combining Mo, Cs Br, and  $\text{Br}_2$  in high-temperature ampoules. Next,  $\text{Cs}^+$  substitution reaction was performed for  $\text{DDA}^+$  in acetone with  $\text{C}_{38}\text{H}_{80}\text{N}^+$ . After that, molybdenum complexes were solved in organic solvents such as dichloromethane and ethyl acetate due to the presence of a cation with two long aliphatic tails. The obtained molybdenum complexes were opted for the first time to catalyze aquathermolysis processes in our study.

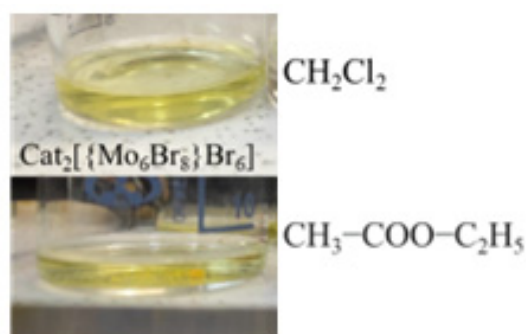
**Table 1.** Physical and chemical properties of initial heavy oil.

Viscosity, @ 20 °C, mPa·s	2802.4		
Density, kg/m <sup>3</sup>	971.8		
API Gravity	14.1		
<b>SARA fractions, wt%</b>			
Saturates	Aromatics	Resins	Asphaltenes
28.05	42.17	22.96	6.82
<b>Elemental analysis, wt%</b>			
Carbon	Hydrogen	Sulfur	Nitrogen
83.48	11.41	4.61	0.38



**Figure 1.** The obtained molybdenum octahedral cluster complexes (Mo OHCs).

The presence of a cation with two long aliphatic tails in the synthesized catalyst can increase the solubility of complexes with different organic solvents such as dichloromethane and ethyl acetate as shown in Figure 2. As can be seen from Figure 2, the catalyst shows a high solubility in organic solvents, which means that the catalyst can be well dispersed in oil.



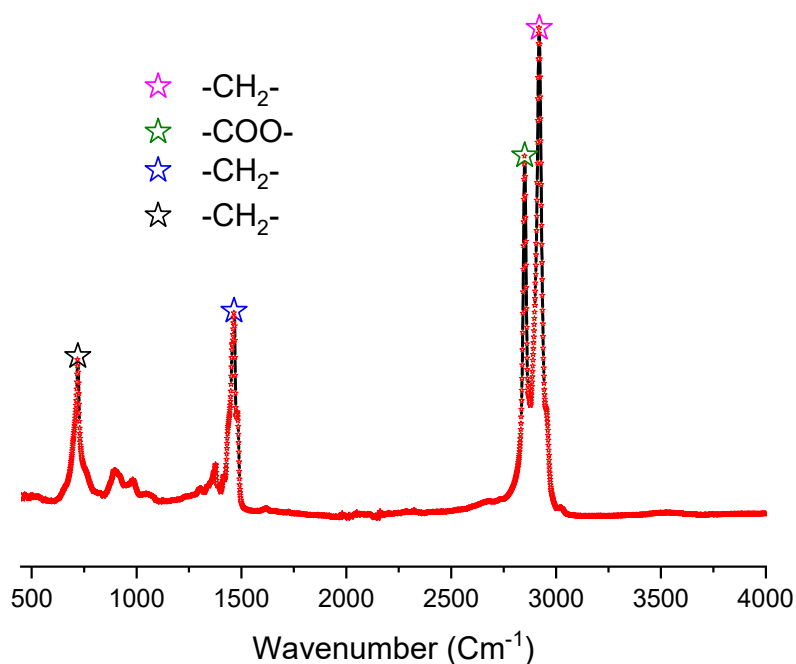
**Figure 2.** Demonstration of the solubility of the catalyst in dichloromethane and ethyl acetate.

### 2.3. Catalysts Characterization

#### 2.3.1. Fourier-Transform Infrared Spectroscopy (FTIR)

One of the most informative and sensitive methods for analyzing the structure of organic compounds is FTIR spectroscopy. A Vertex 70 FTIR spectrometer (Bruker, Germany) was used in this study to determine the structure of the obtained catalyst by taking into consideration the recommendations of Rakhmatullin et al. [30] who documented the procedures and parameters related to obtaining and processing FTIR spectra.

Figure 3 depicts the structure of the MoOHCs catalyst used in heavy oil upgrading prior to the reaction. The presence of monomer compounds, which are methylene molecules, is indicated by the presence of  $\text{CH}_2$  peaks within the boundaries of the functional group region. According to FTIR analysis, high and numerous  $\text{CH}_2$  peaks correlate with the content of organic bonds in the catalyst, which aid in introducing the metal ion to the inner oil phase, enhancing the catalyst's cracking ability.

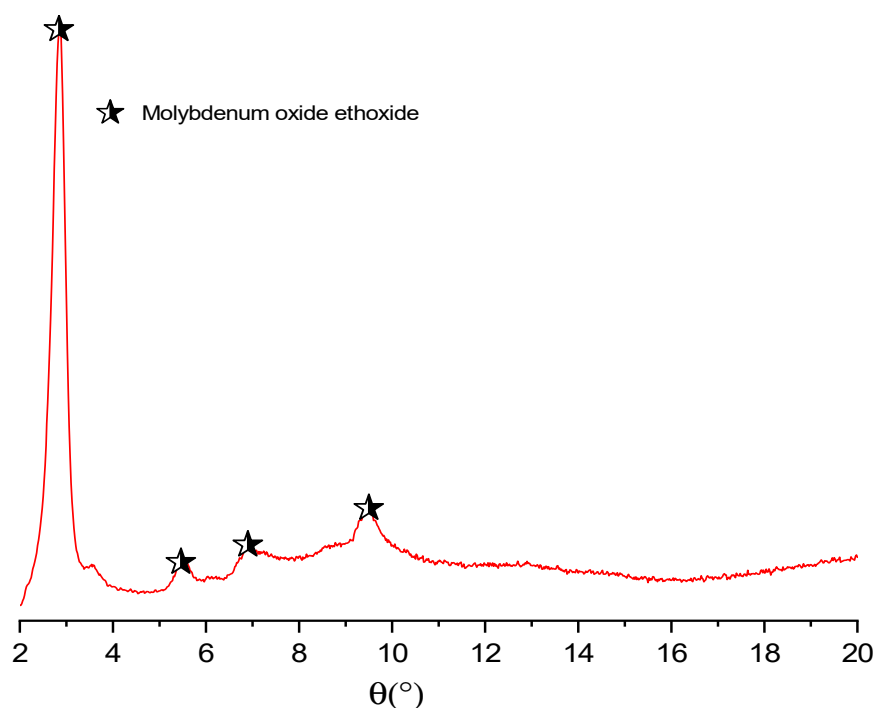


**Figure 3.** FTIR of the obtained molybdenum octahedral cluster complex Mo OHCs.

### 2.3.2. X-ray Diffraction Analysis

The structure of the solid particles of Mo OHCs and the obtained Mo-oxides and sulfides after the aquathermolysis experiment were studied by means of X-ray powder diffraction (XRD) using a desktop MD-10 diffractometer working in the Debye–Scherer geometry with an Fe K $\alpha$  ( $\lambda = 0.193728 \text{ \AA}$ ) radiation tube in order to reveal some reactions' mechanisms and the role of catalysts in upgrading heavy oil by removing metallic elements such as sulfur and others.

The obtained XRPD (Figure 4) showed that the obtained catalyst's content of an organic nature (oxide ethoxide) would promote its dispersion within the volume of the studied oil and would improve its catalytic activity during the process of heavy oil hydrothermal processing and aquathermolysis reactions.



**Figure 4.** XRPD of the obtained molybdenum octahedral cluster complex Mo OHCs.

### 2.3.3. Scanning Electron Microscopy (SEM)

The morphological properties of the obtained particles after the aquathermolysis of heavy oil in the presence of the used catalysts have been investigated by Merlin Carl Zeiss Microscopy. This technique is based on scanning the surface of the obtained solid materials by applying a high-energy electron beam through a thermal field emission type with a stability  $>0.2\%/h$  and a resolution of  $0.8 \text{ nm}$  @  $15 \text{ kV}$ ,  $WD = 8.5 \text{ mm}$ , and a magnification factor of more than  $12\text{--}2,000,000\times$ . At the end of the analysis, solid shape, size, and atomic composition were all determined by the transmitted signals.

## 2.4. Catalyst's Effect on Aquathermolysis Performance

### 2.4.1. Heavy Oil Upgrading in the Presence and Absence of Oil Soluble MoOHCs

In order to evaluate the effect generated by the obtained catalyst on the aquathermolysis performance, we performed a set of heavy oil hydrothermal experiments in a stainless-steel high-pressure autoclave in the presence and absence of MoOHCs at various temperatures of  $200$ ,  $250$ , and  $300^\circ\text{C}$  with  $70:30 \text{ g}$  of oil-to-water ratio, respectively. The mass concentration of the catalyst was about  $0.2 \text{ wt\%}$  by metal. The experiments started initially with nitrogen injection into the reaction medium to create an inert medium with a pressure of  $2 \text{ bar}$ . The reactor was heated at different temperatures ( $200$ ,  $250$  or  $300^\circ\text{C}$ ) with a heating rate of  $5^\circ\text{C}/\text{min}$  and was kept for about  $24 \text{ h}$  at these temperatures for each

experiment. The final pressure reached 20, 30 and 75 bar for the experiments provided at 200, 250 and 300 °C, respectively.

#### 2.4.2. Gas Chromatography Analysis

The Chromatic-Crystal 5000 gas chromatography was used to analyze the evolved gases. The gas separation was carried out at temperatures ranging from 35 to 250 °C using a capillary tube with a length of more than 100 m, a diameter of 0.25 mm, and a heating rate of 2 °C/min. The analysis started with injecting helium at a flow rate of 25 mL/min in order to neutralize any gases from the capillary tube. Gas chromatograph Agilent 7890A with a flame ionization detector and equipped with a capillary column (30 m length) and a diameter of 0.32 mm was used to determine the carbon number distribution of saturated hydrocarbons.

#### 2.4.3. Viscosity Measurement and Elemental Analysis

The Brookfield DV-II + Pro Rotational Viscometer was used to determine the viscosity of heavy oil before and after upgrading in the presence and absence of the used catalyst. Elemental composition (CHNS/O) of heavy oil before and after upgrading in the presence and absence of the catalyst was determined using the Perkin Elmer 2400 Series II Analyzer.

#### 2.4.4. SARA Analysis

SARA analysis of initial heavy oil and upgraded oil after catalytic and non-catalytic hydrothermal processing was carried out by taking into consideration the recommendations of ASTM D 4124 standard. Generally speaking, the oil–heptane ratio of 1:40 was suggested to precipitate the asphaltene for 24 h in a dark medium, which then becomes a mixture of maltene and asphaltene. The asphaltene fraction was then separated from the maltenes using filter paper, and the maltene residue was extracted from the filter paper using an extractor. Finally, maltenes were divided into three components (saturated hydrocarbons, aromatics and resins) using aluminum oxide dry powder in an open column system with heptane, toluene, and a 1:1 mixture of toluene and isopropanol solvents, respectively.

### 3. Results and Discussion

#### 3.1. GC of Evolved Gases

Table 2 shows the results of the evolved gases products after heavy oil upgrading in the presence and absence of MoOHC. The formation of smaller hydrocarbon radicals such as methyl and ethyl because of the random splitting of the side chains caused by free radical reactions increased the light hydrocarbon gases  $\Sigma$ C1–C4 to more than 1.06 wt% in the presence of the oil-soluble octahedral cluster complex of molybdenum catalyst. While it was less than 0.178 wt% in non-catalytic upgrading [31], this indicates that the catalyst has a high-performance degree in upgrading heavy oil. In addition, the content of hydrogen sulfide in the gases increased compared to the non-catalytic upgrading process. This means that the catalyst promotes the hydrodesulfurization reaction of sulfur-containing compounds [11,32]. Moreover, water contributed to the heavy oil upgrading reaction by donating an oxygen atom, resulting in the formation of CO and CO<sub>2</sub> gases [33] as shown in Table 2.

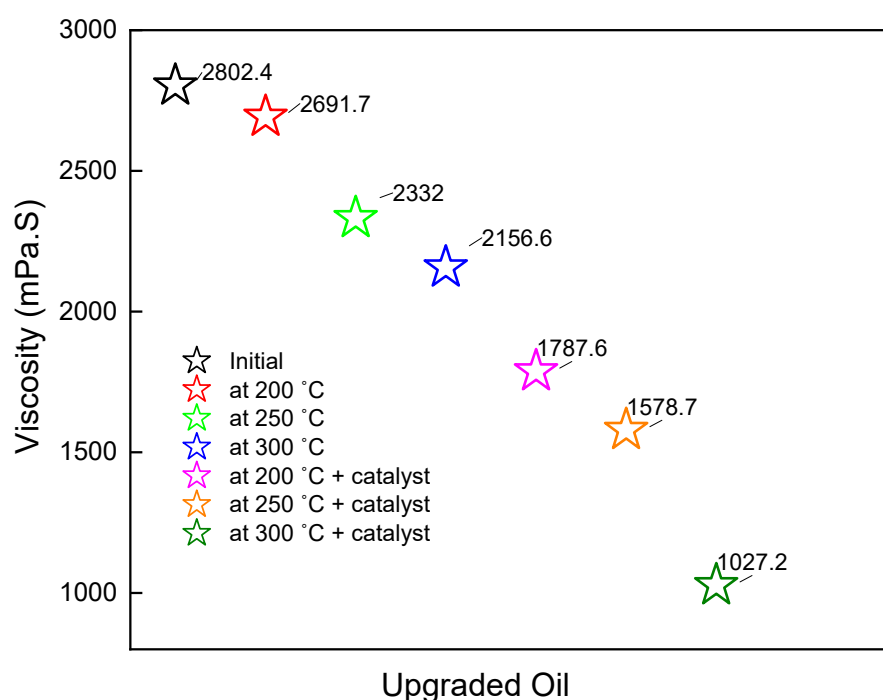
#### 3.2. Viscosity Measurement

The effectiveness and activity of the opted oil-soluble catalyst (octahedral cluster complex of molybdenum) in removing the molecular agglomerations caused by the presence of heavy hydrocarbons such as asphaltenes and resins [34,35] are demonstrated by the results of viscosity measurements of oil after upgrading in the presence of the catalyst (Figure 5). The oil-soluble octahedral molybdenum catalyst cluster complex performed excellently, achieving a viscosity reduction of more than 63%, reducing the viscosity from 2802.4 to 1027.2 mPa·s at 300 °C. Furthermore, in the presence of the catalyst, the content of resins and asphaltenes decreased. As a result, low viscosity refers to the catalyst's ability to

cracking weak bonds such as C-S, C-O and C-C, which lowers viscosity as the molecular weight decreases [36–38].

**Table 2.** Evolved gas products during heavy oil upgrading in the presence and absence of MoOHC.

Compounds	Gas Yields, Mass Percent %					
	Non-Catalytic Upgrading			Catalytic Upgrading		
	200 °C	250 °C	300 °C	200 °C	250 °C	300 °C
ΣC1-C4	0.38432	0.41327	0.51442	0.46445	0.50207	1.06166
H <sub>2</sub> S	0.20572	0.44435	0.66124	0.69171	0.9378	1.29571
H <sub>2</sub>	0.02706	0.18179	0.20325	0.01301	0.05675	0.11953
CO <sub>2</sub>	0.82821	0.85904	0.66482	0.97645	0.81345	0.98701
CO	0.00795	0.01529	0.04893	0.01523	0.0781	0.09151



**Figure 5.** Viscosity measurement at 3.4 cm<sup>-1</sup> share rate before and after catalytic and non-catalytic upgrading of heavy oil at 20 °C.

### 3.3. SARA Analysis

As previously stated, the results in Table 3, show that the octahedral cluster complex of molybdenum catalyst is highly effective and efficient in reducing the heavy compound content of asphaltenes and resins. The oil-soluble catalyst plays two roles in the upgrading of heavy oil: the first one is its high capacity in cracking reactions of long chains with weak bonds such as C–R bonds (R = S, N, and O), which resulted in the conversion of heavy compounds into light compounds [15]; the second role is its ability to improve and stimulate hydrogenation reactions, which led to the stability of the chains that were subjected to cracking by donating hydrogen to them, resulting in the conversion of heavy compounds into light compounds [39]. Furthermore, the best upgrade for heavy oil was achieved at 300 °C, when the content of light compounds increased from 70.22% to 81.55%, indicating the octahedral cluster complex of molybdenum catalyst's superior performance in upgrading heavy oil. In addition, the catalyst contributes to decreasing resin content, especially in the presence of a high amount of hydrogen as a result of hydrogenation reaction stimulation after the cracking reactions of the side chains of heavy compounds [40],



as shown by the obtained amount of saturated hydrocarbons after aquathermolysis in the presence of MoOHC (Table 3).

**Table 3.** SARA analysis of the upgraded heavy oil in the presence and absence of MoOHC catalyst.

SARA of Initial Heavy Oil (wt%)						
Temp. °C	Saturates	Aromatics	Resins	Asphaltenes	Light Components (Sat + Arom)	Heavy Components (Res + Asph)
	28.05	42.17	22.96	6.82	70.22	29.78
SARA Non-Catalytically Upgraded Oil (wt%)						
200 °C	28.79	43.48	20.98	6.75	72.27	27.73
250 °C	29.49	45.11	19.02	6.38	74.60	25.4
300 °C	31.82	43.87	17.95	6.36	75.69	24.31
SARA of Catalytically Upgraded (wt%)						
200 °C	47.03	29.42	17.38	6.17	76.45	23.55
250 °C	47.05	33.50	13.57	5.88	80.55	19.45
300 °C	49.80	31.75	13.66	4.78	81.55	18.44

### 3.4. GC-Analysis

We applied GC analysis so that we could obtain more evidence about the efficiency of the molybdenum-based catalyst. The products were separated based on  $C_{18}$  to ease the comparison, and the carbon numbers were grouped into two parts,  $C_{10}$ – $C_{18}$  corresponding to light distillates (174.1–316 °C), and  $>C_{18}$  for heavy fractions ( $>329$  °C). The carbon number distribution of saturated compounds, which is shown in Table 4, is consistent with SARA analysis data, which showed an increase in saturated hydrocarbon content as a result of a deep conversion of asphaltenes and resins due to cracking, resulting in the separation of alkyl asphalt substitutes in the presence of the oil-soluble catalyst [9]. Furthermore, at different temperatures of 200, 250, and 300 °C in the presence of the catalyst, the content of saturated compounds for the fractions  $C_{10}$ – $C_{18}$  increased gradually to 33.72%, 35.36%, and 38.20%, respectively. Moreover, the content of saturated alkanes  $>C_{18}$  compounds decreased to 61.80% in the presence of the catalyst at 300 °C, compared to 70.71% in the initial saturated compound. This indicates that long chains of resin and asphaltene were cracked, de-alkylated, and hydrogenated, resulting in the cleavage of many C-C, C-N, and C-S bonds [41], leading to a rise in the content of light alkanes.

### 3.5. Elemental Analysis

The results of the elemental analysis (S, O, and N) of the initial and upgraded oil in the presence and absence of the molybdenum-based catalyst are shown in Table 5. The results showed that the catalyst performed admirably in removing sulfur, with a sulfur removal rate of 26% at 300 °C. The ability of the catalyst in the desulfurization reactions is linked to the weak C–S bonds that are abundant in the content of asphaltenes and resins, where the cleavage of these bonds led to a decrease in the sulfur content in the upgraded oil [41]. In addition, the presence of the molybdenum-based octahedron cluster complex improved the catalyst's activity in the hydrogenation and cracking reactions of the weak C–C bonds in heavy hydrocarbons [42,43]. This increased the H content, decreased the C content, and increased the H/C ratio from 1.64 to 1.72 at 300 °C. In addition, the N content was not significantly reduced because C–N bonds, which are found in resins and asphaltenes, are among the most stable bonds in oil [44]. Thus, bond cleavages (C–S, C–N and C–C) reduced the total number of rings after releasing the light components and increased the content of light compounds from saturated and aromatic compounds in the presence of the catalyst. As a result, the viscosity of the upgraded oil significantly decreased and improved the oil's flow characteristics [40].

**Table 4.** Carbon number distribution percentage before and after catalytic and non-catalytic upgrading.

Temp. °C	Initial Heavy Oil Distribution, %	
	C <sub>10</sub> –C <sub>18</sub> 29.28	>C <sub>18</sub> 70.71
<b>Non-Catalytic Upgrading Distribution %</b>		
200	29.78	70.21
250	31.46	68.53
300	34.18	65.81
<b>Mo OHCs—Catalytic Upgrading Distribution %</b>		
200	33.72	66.28
250	35.36	64.63
300	38.20	61.80

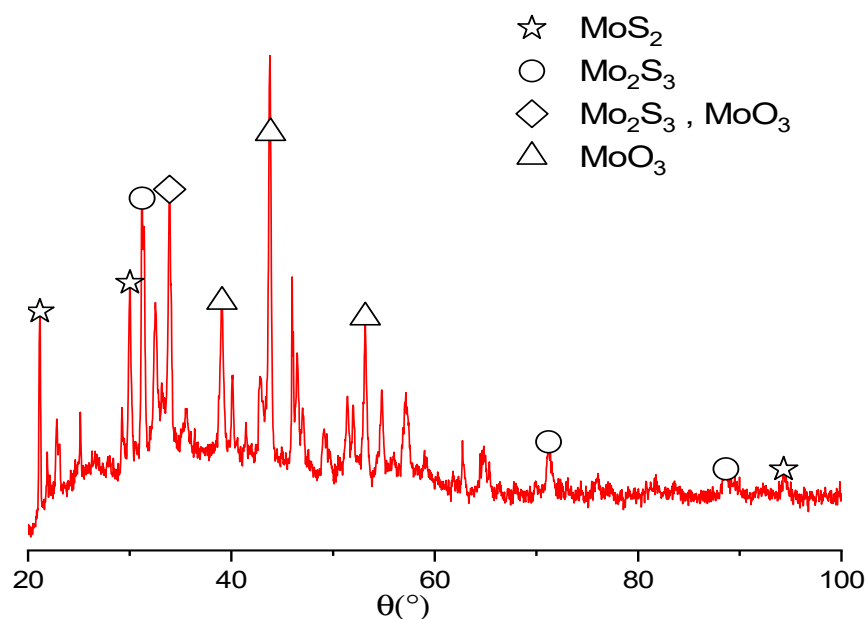
**Table 5.** Elemental analysis of oil before and after upgrading in the presence and absence of MoOC catalyst.

Sample	C	H	N	S	O	H/C Ratio	Sulfur Removal (%)
Initial heavy oil	83.48	11.41	0.38	4.61	0.12	1.644	-
Non-catalytic—200 °C	83.37	11.47	0.35	4.47	0.34	1.651	3.03
Non-catalytic—250 °C	83.18	11.49	0.35	4.22	0.76	1.664	8.45
Non-catalytic—300 °C	83.15	11.49	0.34	4.17	0.85	1.658	9.54
Mo OHCs—upgrading—200 °C	82.69	11.46	0.34	4.21	1.30	1.663	8.68
Mo OHCs—upgrading—250 °C	82.64	11.71	0.31	3.68	1.66	1.700	20.17
Mo OHCs—upgrading—300 °C	82.43	11.87	0.28	3.41	2.01	1.728	26.03

### 3.6. X-ray Diffraction of the Obtained Solids after Heavy Oil Catalytic Upgrading

The results of XRD showed that the used catalysts decomposed and transformed into particles of Mo sulfide and Mo oxide under thermal cracking effects, as shown in XRD patterns (Figure 6). This tends toward the fact that the oil-soluble catalyst decomposed during the process of hydrothermal processing of heavy oil in the presence of water into molybdenum sulfides during hydrodesulfurization reactions that occurred with heavy oil upgrading, which corresponds to the gas chromatography analysis that revealed the presence of H<sub>2</sub>S gas with the gases produced during heavy oil upgrading in the presence of the catalyst.

The active form of the obtained Mo-based catalyst after thermal processing was explained in detail in our previous work [8] where the obtained results have confirmed the crucial role played by the formed Mo oxides in breaking down high-molecular weight hydrocarbon components (resins and asphaltenes) into light hydrocarbon compounds (saturates and aromatics) under the catalytic thermal effect [45–47]. Furthermore, Mo sulfide was found to be an intermediate product in the thermocatalytic conversion of sulfur-containing hydrocarbons in heavy oil as a result of thermocatalytic decomposition in the presence of water (steam). During catalytic thermal decomposition under the influence of metal oxide, some metal ions react preferentially with sulfurous components, creating sulfide metal, which can be crucial during the hydrodesulfurization of heavy crude oil. In addition, the sulfide metal aids in the splitting of water into hydrogen. Moreover, the generated hydrogen then participates in the hydrogenation process and contributes in eliminating the free radicals that were formed by reacting with sulfur compounds to produce H<sub>2</sub>S [27,48].



**Figure 6.** XRPD of the obtained Mo-based catalyst after thermal processing.

### 3.7. SEM-EDX Analysis

The composition of the catalyst surface after catalytic upgrading experiments in the presence of Mo OHCs is shown in Figure 7. The SEM image shows that the sizes of the catalyst particles were 8–10  $\mu\text{m}$ , which remained in the same size range after the reaction. The carbohydrate and carbonate molecules that formed due to the loss of alkyl substituents after the asphaltene molecules' cracking are the reasons behind the composition formed on the catalyst surface after catalytic upgrading.

### 3.8. Comparative Study of the Obtained Results with Literature Data

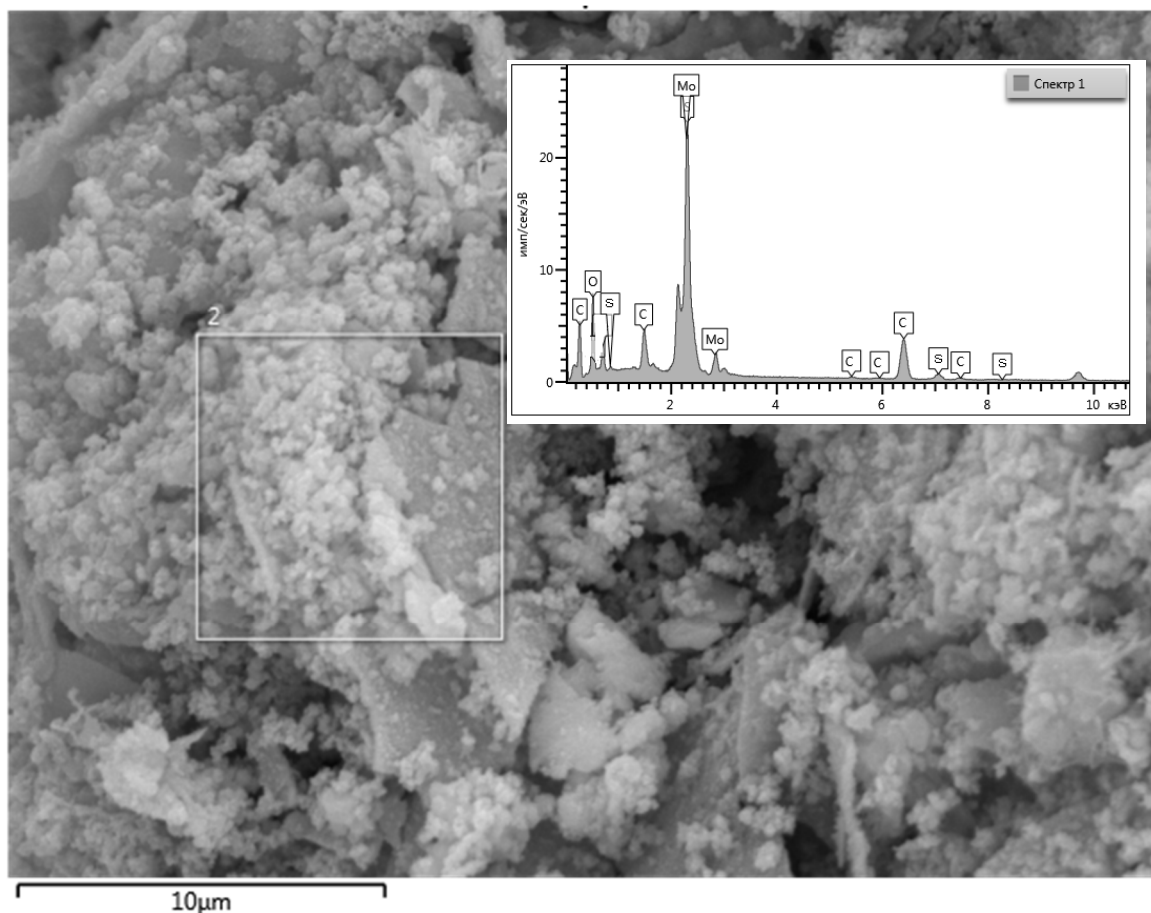
Table 6 provides a comparative study between the obtained data in the present work and previously published data about the application of molybdenum-based catalysts in the field of hydrothermal processing of heavy oil and feedstock.

**Table 6.** Comparative analysis of the results of different studies based on Mo.

Catalyst Type	Reaction Temp. °C	Sat. Raising %	Res. Reduction %	Asph. Reduction %	Viscosity Reduction %	Sulfur Removal %	H/C Ratio
Mo OHCs	300	43.7	40.50	30.0	63	26.03	1.728
[18] $\text{MoO}_2(\text{acac})_2$	410	-	-	21.0	43.0	16.0	1.48
[49] $\text{MoO}_3$	300	-	-	-	22.59	15.14	-
[50] Ni-Mo/ $\text{Al}_2\text{O}_3$	350	-	-	28.0	59.0	21.60	-
[51] $\text{Mo}(\text{CO})_6$	415	24.8	14.8	40.9	-	31.70	-
[51] $\text{MoS}_2$	415	7.5	25.0	25.0	-	16.01	-

Table 6 shows the efficiency of the opted catalyst in our study (Mo OHCs). It is seen that the amount of saturates that increases reaches 43.7% in the presence of the used catalyst compared to 24.8% in the presence of  $\text{Mo}(\text{CO})_6$  and 7.5% in the presence of  $\text{MoS}_2$ . Moreover, the amount of asphaltenes decreased significantly in the presence of Mo OHCs (30%) compared to 21% ( $\text{MoO}_2(\text{acac})_2$ ), 28% (Ni-Mo/ $\text{Al}_2\text{O}_3$ ) and 25% ( $\text{MoS}_2$ ). Additionally, MoOHCs decreased the produced oil viscosity by 63%, which was found to be the maximum value compared to other catalysts. Furthermore, the efficiency of the used

catalyst was reflected by the significant amount of sulfur removal from the produced oil by 26.03%.



**Figure 7.** SEM-EDX image of the obtained particles from MoOHcs decomposition during heavy oil upgrading process.

The obtained data within the present work are promising and should be validated by larger scale samples.

#### 4. Conclusions

To sum up, our study applied for the first-time molybdenum-based oil-soluble catalysts in upgrading heavy oil via aquathermolysis. We synthesized a molybdenum-based octahedron cluster complex,  $(C_{38}H_{80}N)_2[Mo_6Br_8]Br_6$ , and studied its physical and morphological properties by using a variety of physical and chemical methods. The obtained catalyst was tested in the process of heavy oil aquathermolysis upgrading in a batch reactor at different temperatures (250, 300 and 350 °C) for 24 h. The obtained data demonstrated high efficiency and activity of the obtained catalyst in upgrading heavy oil by reducing viscosity at 200, 250, and 300 °C, with more than 63% at 300 °C in the presence of a 0.1% by-metal catalyst content. As a result of cracking and hydrogenation reactions of long side chains of heavy compounds, the content of heavy hydrocarbons in resins and asphaltenes decreased to less than 18.44% at 300 °C from 29.78% before upgrading. This resulted in a significant increase in the content of light fractions C10–C18 from 29.28% to more than 38%. The XRD, elemental analysis, and gas chromatography results showed a higher efficiency of the opted catalyst in the reactions of desulfurization, where elemental analysis revealed a significant decrease in sulfur content of the upgraded oil in the presence of the catalyst. However, XRD analysis of the obtained particles revealed a higher content of sulfur on their surface, which confirms the high activity of the used catalyst in desulfurization. Moreover,

the presence of H<sub>2</sub>S gas as one of the gases produced during heavy oil upgrading indicates the catalyst's high ability to crack weak S-containing bonds (C-S), as well as the catalyst's role in hydrogenation reactions that increased the content of saturated compounds.

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## References

1. Ngô, C.; Natowitz, J. *Our Energy Future: Resources, Alternatives and the Environment*; John Wiley & Sons: Hoboken, NJ, USA, 2016; ISBN 1119213363.
2. Maganov, N.; Ibragimov, N.; Khisamov, R.; Zaripov, A.; Motina, L.; Mekheev, E. Experience of Development of Shallow Deposits of Heavy Oil. *Oil Gas J. Russ.* **2015**, *5*, 60–63.
3. Peker, B.O. The Opportunities and Limits of Bioenergy for a Sustainable Energy System in Turkey. Master's Thesis, Lappeenranta University of Technology, Lappeenranta, Finland, 2016.
4. Djimasbe, R.; Varfolomeev, M.A.; Al-Muntaser, A.A.; Yuan, C.; Feoktistov, D.A.; Suwaid, M.A.; Kirgizov, A.J.; Davletshin, R.R.; Zinnatullin, A.L.; Fatou, S.D. Oil Dispersed Nickel-Based Catalyst for Catalytic Upgrading of Heavy Oil Using Supercritical Water. *Fuel* **2022**, *313*, 122702. [[CrossRef](#)]
5. Ancheyta, J.; Speight, J.G. Heavy Oils and Residua. In *Hydroprocessing Heavy Oils Residua*; CRC Press: Boca Raton, FL, USA, 2007.
6. Romanov, G.V. The Objective Republican Program for the Heavy Oils and Natural Bitumen Fields Integrated Development in the Territory of the Republic of Tatarstan. *Georesursy* **2012**, *46*, 34–37.
7. Tumanyan, B.P.; Romanov, G.V.; Nurgaliev, D.K.; Kayukova, G.P.; Petrukhina, N.N. Promising Aspects of Heavy Oil and Native Asphalt Conversion under Field Conditions. *Chem. Technol. Fuels Oils* **2014**, *50*, 185–188. [[CrossRef](#)]
8. Suwaid, M.A.; Varfolomeev, M.A.; Al-Muntaser, A.A.; Abdaljalil, N.I.; Djimasbe, R.; Rodionov, N.O.; Zinnatullin, A.; Vagizov, F.G. Using the Oil-Soluble Copper-Based Catalysts with Different Organic Ligands for in-Situ Catalytic Upgrading of Heavy Oil. *Fuel* **2022**, *312*, 122914. [[CrossRef](#)]
9. Suwaid, M.A.; Varfolomeev, M.A.; Al-Muntaser, A.A.; Yuan, C.; Starshinova, V.L.; Zinnatullin, A.; Vagizov, F.G.; Rakhmatullin, I.Z.; Emelianov, D.A.; Chemodanov, A.E. In-Situ Catalytic Upgrading of Heavy Oil Using Oil-Soluble Transition Metal-Based Catalysts. *Fuel* **2020**, *281*, 118753. [[CrossRef](#)]
10. Sitnov, S.A.; Khelkhal, M.A.; Mukhamatdinov, I.I.; Feoktistov, D.A.; Vakhin, A.V. Iron Oxide Nanoparticles Impact on Improving Reservoir Rock Minerals Catalytic Effect on Heavy Oil Aquathermolysis. *Fuel* **2022**, *327*, 124956. [[CrossRef](#)]
11. Maity, S.K.; Ancheyta, J.; Marroquín, G. Catalytic Aquathermolysis Used for Viscosity Reduction of Heavy Crude Oils: A Review. *Energy Fuels* **2010**, *24*, 2809–2816. [[CrossRef](#)]
12. Galukhin, A.; Nosov, R.; Eskin, A.; Khelkhal, M.; Osin, Y. Manganese Oxide Nanoparticles Immobilized on Silica Nanospheres as a Highly Efficient Catalyst for Heavy Oil Oxidation. *Ind. Eng. Chem. Res.* **2019**, *58*, 8990–8995. [[CrossRef](#)]
13. Khelkhal, M.A.; Lapuk, S.E.; Buzyurov, A.V.; Ignashev, N.E.; Shmeleva, E.I.; Mukhamatdinov, I.I.; Vakhin, A.V. Thermal Behavior of Heavy Oil Catalytic Pyrolysis and Aquathermolysis. *Catalysts* **2022**, *12*, 449. [[CrossRef](#)]
14. Speight, J.G. New Approaches to Hydroprocessing. *Catal. Today* **2004**, *98*, 55–60. [[CrossRef](#)]
15. Al-Attas, T.A.; Ali, S.A.; Zahir, M.H.; Xiong, Q.; Al-Bogami, S.A.; Malaibari, Z.O.; Razzak, S.A.; Hossain, M.M. Recent Advances in Heavy Oil Upgrading Using Dispersed Catalysts. *Energy Fuels* **2019**, *33*, 7917–7949. [[CrossRef](#)]
16. Bdwi, E.A.S.; Ali, S.A.; Quddus, M.R.; Al-Bogami, S.A.; Razzak, S.A.; Hossain, M.M. Kinetics of Promotional Effects of Oil-Soluble Dispersed Metal (Mo, Co, and Fe) Catalysts on Slurry Phase Hydrocracking of Vacuum Gas Oil. *Energy Fuels* **2017**, *31*, 3132–3142. [[CrossRef](#)]

17. Petrukhina, N.N.; Sizova, I.A.; Maksimov, A.L. Nickel–Molybdenum and Cobalt–Molybdenum Sulfide Hydrogenation and Hydrodesulphurization Catalysts Synthesized in Situ from Bimetallic Precursors. *Catal. Ind.* **2017**, *9*, 247–256. [[CrossRef](#)]
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*, 379–385. [[CrossRef](#)]
19. Brorson, M.; Carlsson, A.; Topsøe, H. The Morphology of MoS<sub>2</sub>, WS<sub>2</sub>, Co–Mo–S, Ni–Mo–S and Ni–W–S Nanoclusters in Hydrodesulfurization Catalysts Revealed by HAADF-STEM. *Catal. Today* **2007**, *123*, 31–36. [[CrossRef](#)]
20. Kim, S.-H.; Kim, K.-D.; Lee, Y.-K. Effects of Dispersed MoS<sub>2</sub> Catalysts and Reaction Conditions on Slurry Phase Hydrocracking of Vacuum Residue. *J. Catal.* **2017**, *347*, 127–137. [[CrossRef](#)]
21. Du, H.; Liu, D.; Li, M.; Wu, P.; Yang, Y. Effects of the Temperature and Initial Hydrogen Pressure on the Isomerization Reaction in Heavy Oil Slurry-Phase Hydrocracking. *Energy Fuels* **2015**, *29*, 626–633. [[CrossRef](#)]
22. Galukhin, A.V.; Erokhin, A.A.; Osin, Y.N.; Nurgaliev, D.K. Catalytic Aquathermolysis of Heavy Oil with Iron Tris (Acetylacetonate): Changes of Heavy Oil Composition and in Situ Formation of Magnetic Nanoparticles. *Energy Fuels* **2015**, *29*, 4768–4773. [[CrossRef](#)]
23. Al-Attas, T.A.; Zahir, M.H.; Ali, S.A.; Al-Bogami, S.A.; Malaibari, Z.; Razzak, S.A.; Hossain, M.M. Novel (Co-, Ni)-p-Tert-Butylcalix [4] Arenes as Dispersed Catalysts for Heavy Oil Upgrading: Synthesis, Characterization, and Performance Evaluation. *Energy Fuels* **2018**, *33*, 561–573. [[CrossRef](#)]
24. Daage, M.; Chianelli, R.R. Structure-Function Relations in Molybdenum Sulfide Catalysts: The “Rim-Edge” Model. *J. Catal.* **1994**, *149*, 414–427. [[CrossRef](#)]
25. Kang, K.H.; Nguyen, N.T.; Seo, P.W.; Seo, H.; Kim, G.T.; Kang, N.; Lee, C.W.; Han, S.J.; Chung, M.-C.; Park, S. Slurry-Phase Hydrocracking of Heavy Oil over Mo Precursors: Effect of Triphenylphosphine Ligands. *J. Catal.* **2020**, *384*, 106–121. [[CrossRef](#)]
26. Chen, Z.; Cao, Y.; Ma, Y.; Au, C.; Jiang, L.; Bao, X. Synthesis, Characterization, and Catalytic Performance of Aminomethylphosphonic Molybdenum Catalysts for Slurry-Phase Hydrocracking. *Ind. Eng. Chem. Res.* **2019**, *58*, 2689–2696. [[CrossRef](#)]
27. 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*, 108335. [[CrossRef](#)]
28. Yusuf, A.; Al-Hajri, R.S.; Al-Waheibi, Y.M.; Jibril, B.Y. Upgrading of Omani Heavy Oil with Bimetallic Amphiphilic Catalysts. *J. Taiwan Inst. Chem. Eng.* **2016**, *67*, 45–53. [[CrossRef](#)]
29. Kirakci, K.; Cordier, S.; Perrin, C. Synthesis and Characterization of Cs<sub>2</sub>Mo<sub>6</sub>X<sub>14</sub> (X = Br or I) Hexamolybdenum Cluster Halides: Efficient Mo<sub>6</sub> Cluster Precursors for Solution Chemistry Syntheses. *Zeitschrift Anorg. und Allg. Chemie* **2005**, *631*, 411–416. [[CrossRef](#)]
30. Rakhmatullin, I.Z.; Efimov, S.V.; Tyurin, V.A.; Al-Muntaser, A.A.; Klimovitskii, A.E.; Varfolomeev, M.A.; Klochkov, V.V. Application of High Resolution NMR (<sup>1</sup>H and <sup>13</sup>C) and FTIR Spectroscopy for Characterization of Light and Heavy Crude Oils. *J. Pet. Sci. Eng.* **2018**, *168*, 256–262. [[CrossRef](#)]
31. 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. Hydrogen Donating Capacity of Water in Catalytic and Non-Catalytic Aquathermolysis of Extra-Heavy Oil: Deuterium Tracing Study. *Fuel* **2021**, *283*, 118957. [[CrossRef](#)]
32. Aliev, F.A.; Mukhamatdinov, I.I.; Sitnov, S.A.; Ziganshina, M.R.; Onishchenko, Y.V.; Sharifullin, A.V.; Vakhin, A.V. In-Situ Heavy Oil Aquathermolysis in the Presence of Nanodispersed Catalysts Based on Transition Metals. *Processes* **2021**, *9*, 127. [[CrossRef](#)]
33. Sato, T.; Mori, S.; Watanabe, M.; Sasaki, M.; Itoh, N. Upgrading of Bitumen with Formic Acid in Supercritical Water. *J. Supercrit. Fluids* **2010**, *55*, 232–240. [[CrossRef](#)]
34. Muraza, O. Hydrous Pyrolysis of Heavy Oil Using Solid Acid Minerals for Viscosity Reduction. *J. Anal. Appl. Pyrolysis* **2015**, *114*, 1–10. [[CrossRef](#)]
35. Kapadia, P.R.; Kallos, M.S.; Gates, I.D. A New Reaction Model for Aquathermolysis of Athabasca Bitumen. *Can. J. Chem. Eng.* **2013**, *91*, 475–482. [[CrossRef](#)]
36. Li, J.; Wang, X.; Tang, X.; Wang, F.; Qing, D. Effect of Transition Metal Polymers with Varying Side Alkyl Chain on Viscosity Reduction of Crude Oil and Aggregation Behavior of Asphaltene. *Energy Fuels* **2015**, *29*, 7771–7780. [[CrossRef](#)]
37. Chuan, W.U.; Guang-Lun, L.E.I.; YAO, C.; SUN, K.; Gai, P.; CAO, Y. Mechanism for Reducing the Viscosity of Extra-Heavy Oil by Aquathermolysis with an Amphiphilic Catalyst. *J. Fuel Chem. Technol.* **2010**, *38*, 684–690.
38. Chen, E.Y.; Liu, Y.J.; Liang, M.; WU, H.; HAN, C. A Study on the Viscosity Reduction of Liaohe Heavy Oil by Oil-Soluble Nickel Oleate. *J. Daqing Pet. Inst.* **2010**, *34*, 68–71.
39. Vakhin, A.V.; Sitnov, S.A.; Mukhamatdinov, I.I.; Aliev, F.A.; Kudryashov, S.I.; Afanasiev, I.S.; Petrashov, O.V.; Varfolomeev, M.A.; Nurgaliev, D.K. Aquathermolysis of Heavy Oil in Reservoir Conditions with the Use of Oil-Soluble Catalysts: Part III—Changes in Composition Resins and Asphaltenes. *Pet. Sci. Technol.* **2018**, *36*, 1857–1863. [[CrossRef](#)]
40. Qin, W.L.; Xiao, Z.L. The Researches on Upgrading of Heavy Crude Oil by Catalytic Aquathermolysis Treatment Using a New Oil-Soluble Catalyst. *Adv. Mater. Res.* **2013**, *608*, 1428–1432. [[CrossRef](#)]
41. Yongjian, L.; Eryue, C.; Shoubin, W. The Preparation and Evaluation of Oil-Soluble Catalyst for Aquathermolysis of Heavy Oil. *Chem. Eng. Oil Gas* **2005**, *6*, 511–512.
42. Hyne, J.B.; Clark, P.D.; Clarke, R.A.; Koo, J.; Greidanus, J.W. Aquathermolysis of Heavy Oils. *Rev. Tec. INTEVEP* **1982**, *2*, 87–94.
43. Wang, Y.; Chen, Y.; He, J.; Li, P.; Yang, C. Mechanism of Catalytic Aquathermolysis: Influences on Heavy Oil by Two Types of Efficient Catalytic Ions: Fe<sup>3+</sup> and Mo<sup>6+</sup>. *Energy Fuels* **2010**, *24*, 1502–1510. [[CrossRef](#)]
44. Ji, L.; Yan, Y.; Dong, C. Morphology Analysis of Resin and Asphaltene. *Chem. Eng. Oil Gas* **2010**, *39*, 454–456.

45. Hosseinpour, M.; Fatemi, S.; Ahmadi, S.J. Deuterium Tracing Study of Unsaturated Aliphatics Hydrogenation by Supercritical Water in Upgrading Heavy Oil. Part II: Hydrogen Donating Capacity of Water in the Presence of Iron (III) Oxide Nanocatalyst. *J. Supercrit. Fluids* **2016**, *110*, 75–82. [[CrossRef](#)]
46. Kosari, M.; Golmohammadi, M.; Ahmadi, S.J.; Towfighi, J.; Chenari, A.H. On the Catalysis Capability of Transition Metal Oxide Nanoparticles in Upgrading of Heavy Petroleum Residue by Supercritical Water. *J. Supercrit. Fluids* **2017**, *126*, 14–24. [[CrossRef](#)]
47. Dejhosseini, M.; Aida, T.; Watanabe, M.; Takami, S.; Hojo, D.; Aoki, N.; Arita, T.; Kishita, A.; Adschiri, T. Catalytic Cracking Reaction of Heavy Oil in the Presence of Cerium Oxide Nanoparticles in Supercritical Water. *Energy Fuels* **2013**, *27*, 4624–4631. [[CrossRef](#)]
48. Khoshooei, M.A.; Elahi, S.M.; Carbognani, L.; Scott, C.E.; Pereira-Almao, P. Activity Assessment of NiMo Bimetallic Nanocatalyst in Presence and Absence of Steam in In-Situ Upgrading Technology (ISUT). *Fuel* **2021**, *288*, 119664. [[CrossRef](#)]
49. Shuwa, S.M.; Al-Hajri, R.S.; Jibril, B.Y.; Al-Waheibi, Y.M. Novel Deep Eutectic Solvent-Dissolved Molybdenum Oxide Catalyst for the Upgrading of Heavy Crude Oil. *Ind. Eng. Chem. Res.* **2015**, *54*, 3589–3601. [[CrossRef](#)]
50. Hart, A.; Wood, J.; Greaves, M. In Situ Catalytic Upgrading of Heavy Oil Using a Pelletized Ni-Mo/Al<sub>2</sub>O<sub>3</sub> Catalyst in the THAI Process. *J. Pet. Sci. Eng.* **2017**, *156*, 958–965. [[CrossRef](#)]
51. Zhu, X.; Qiao, D.; Yang, L.; Bi, Q.; Xing, H.; Ni, S.; Yuan, M.; Liu, H.; Wang, L.; Ma, A. Novel Magnetic Carbon Supported Molybdenum Disulfide Catalyst and Its Application in Residue Upgrading. *Green Energy Environ.* **2021**, *6*, 952–960. [[CrossRef](#)]