Synthesis of Nickel–Tungsten Sulfide Hydrodearomatization Catalysts by the Decomposition of Oil-Soluble Precursors

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Abstract—Nickel-tungsten sulfide catalysts for the hydrogenation of aromatic hydrocarbons have been prepared by the in situ decomposition of an oil-soluble tungsten hexacarbonyl precursor in a hydrocarbon feedstock using oil-soluble nickel salt nickel(II) 2-ethylhexanoate as a source of nickel. The in situ synthesized Ni–W–S catalyst has been characterized by X-ray photoelectron spectroscopy. The activity of the resulting catalysts has been studied in the hydrogenation of bicyclic aromatic hydrocarbons and dibenzothiophene conversion in a batch reactor at a temperature of 350° C and a hydrogen pressure of 5.0 MPa. It has been shown that the optimum W : Ni molar ratio is 1 : 2. Using the example of the hydrofining of feedstock with high sulfur and aromatics contents, it has been shown that the synthesized catalyst exhibits high activity in the hydrogenation of aromatic hydrocarbons.

Keywords: tungsten hexacarbonyl, oil-soluble precursors, nickel-tungsten sulfide catalyst, dehydrodearomatization, light cycle oil

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The use of heavy oil fractions with a high concentration of sulfur and aromatic hydrocarbons (HCs) in oil refining, along with tightening the requirements on the amount of these compounds in fuels, has given an impetus to increased interest in the study of new sulfur-resistant catalysts for the hydrogenation of aromatic compounds. Owing to the exceptional resistance to catalyst poisons, transition metal sulfides [1]—mostly tungsten and molybdenum sulfides promoted with cobalt or nickel-are extensively used in hydrotreating and hydrofining processes involving purification of feedstocks for the removal of impurities containing hetero atoms, such as sulfur, nitrogen, and oxygen, in a hydrogen atmosphere, the hydrogen saturation of unsaturated HCs, and the hydrogenation of aromatic compounds [2].

In recent years, unsupported sulfide catalysts have attracted much attention owing to their high activity in hydrotreatment reactions [3-4]. These catalysts have exhibited higher catalytic activity than conventional supported catalysts [4]. The synthesis methods for unsupported catalysts can be divided into two main groups: the first group involves the synthesis of an active catalyst outside of the reaction zone (ex situ), while the second group is based on the formation of a catalyst directly in a HC medium (in situ). The in situ preparation of a catalyst in the reaction medium provides a high sulfur content in the resulting sulfide catalyst and leads to the formation of stable fine particles [5–9]. Oil-soluble salts, such as transition metal naphthenates, carbonyls, 2-ethylhexanoates, and acetylacetonates, can be used as precursors of sulfide catalysts [10]. Oil-soluble precursors are readily dispersed in a HC feedstock and generate catalysts with high hydrogenation ability. The general scheme of synthesis of sulfide catalysts from oil-soluble precursors distributed in a HC phase includes the thermal decomposition of the precursor in a HC medium with a sulfiding agent [11].

Unlike the well documented Co(Ni)–Mo [3, 9] and Co(Ni)–Mo–W sulfide systems [12, 13], unsupported Ni–W–S catalysts, which must exhibit a substantially higher hydrogenation activity, have been examined to a lesser extent [14] and studies of dispersed catalysts focus on their behavior in the hydrodesulfurization [13–15] and hydroconversion of heavy feedstock [16, 17].

In this study, we propose a method for synthesizing a nickel-tungsten sulfide catalyst by the in situ decomposition of the oil-soluble tungsten hexacarbonyl precursor in a HC feedstock. The catalytic properties in the hydrogenation reaction were studied using model systems (naphthalene and alkyl-substituted naphthalenes with one, two, and three methyl substituents) as an example and in the hydrofining of light cycle oil (LCO), representative actual feedstock with high sulfur and aromatics contents.

Catalyst Synthesis Procedures

The nickel-tungsten sulfide catalyst was prepared in situ in a HC feedstock using the oil-soluble salt tungsten hexacarbonyl $W(CO)_6$ (99.99%, Aldrich) as a precursor and the oil-soluble salt nickel(II) 2-ethylhexanoate Ni(C₇H₁₅COO)₂ (a 78% solution in 2-ethylhexanoic acid, Aldrich) as a source of nickel. To prepare tungsten sulfide exhibiting activity in the hydrogenation of aromatic HCs, 2.5 wt % elemental sulfur was admixed as a sulfiding agent to the HC feedstockwith.

Catalyst Investigation Procedures

X-ray photoelectron spectroscopy (XPS) studies of the resulting samples were conducted using a Kratos Axis Ultra DLD X-ray photoelectron spectrometer. Photoemission was excited using nonmonochromatized AlK α radiation ($h\nu = 1486.6$ eV) with a power of 300 W. Photoelectron peaks were calibrated against the carbon C 1s line with a binding energy of 285 eV. The spectra were deconvoluted by the nonlinear leastsquare method using the Gaussian–Lorentzian function.

Catalytic Testing Procedure

Catalytic hydrogenation tests were conducted in a steel autoclave in a hydrogen atmosphere under a high pressure and vigorous stirring of the reaction mixture. Tungsten hexacarbonyl and nickel(II) 2-ethylhexanoate were dissolved in the HC feedstock. The tungsten content in the feedstock was calculated using the following formula

W =
$$\frac{m(W(CO)_6)M(W)}{M(W(CO)_6)m(feedstock)} \times 10^6 \text{ [ppm]},$$

where $m(W(CO)_6)$ is the mass of tungsten hexacarbonyl dissolved in the HC feedstock, g; M(W) is the molar mass of tungsten, 183.8 g/mol; $M(W(CO)_6)$ is the molar mass of tungsten hexacarbonyl, 351.9 g/mol; and m(feedstock) is the mass of the HC feedstock, g.

Two milliliters of the resulting solution was placed into the glass cartridge of the autoclave. After that, the autoclave was filled with hydrogen to a pressure of 50 atm and held at a temperature of 350° C for 2–10 h; the hydrogen/substrate molar ratio was 60 mol/mol.

Model feedstocks (10% solutions of bicyclic aromatic HCs in benzene) and light gas oil produced on a catalytic cracking unit (LCO) were used in the experiments.

Product Analysis

The hydrogenation products of the model systems were analyzed on a 4000 M Kristallyuks chromatograph equipped with a flame ionization detector and a SPB-1 capillary column coated with the polydimethylsiloxane stationary liquid phase (dimensions, $30 \text{ m} \times$ 0.25 mm; carrier gas, helium; split ratio, 1:90). Conversion was calculated as the degree of conversion of the original aromatic compound to the hydrogenated form. Selectivity was calculated as the ratio of the mass of a given product to the total mass of the resulting products. In some cases, the activities of the catalyst systems were compared in terms of specific catalytic activity (SCA), which is a conventional quantity calculated as the ratio of the amount of the reacted naphthalene to the charge of the catalytically active metal (W), both in moles, per unit time:

SCA =
$$\frac{(5Conv \cdot S(C_{10}H_{18}) + 2Conv \cdot S(C_{10}H_{12}))n(C_{10}H_{8})}{\tau n(W)} [h^{-1}],$$

where *Conv* is the naphthalene conversion; *S* is the reaction product selectivity; $n(C_{10}H_8)$ is the naphthalene content in the original feedstock, mol; n(W) is the charge of the active metal, mol; and τ is the reaction time, h.

The total sulfur analysis of the LCO hydrofining products was conducted on an EA 3100 instrument equipped with an UV detector. The aromatic HC content was determined by HPLC according to GOST R EN 12916-06 (mobile phase, *n*-heptane; amino column, diasphere-80-amine).

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RESULTS AND DISCUSSION

Catalyst Characteristics

XPS analysis of the synthesized catalyst has shown that the spectra exhibit peaks characteristic of tungsten, sulfur, carbon, nickel, nitrogen, and oxygen. The tungsten is in three forms: sulfide (W $4f_{7/2}$, 32.2 eV; W $4f_{5/2}$ 34.3 eV), oxysulfide (W $4f_{7/2}$ 33.4 eV; W $4f_{5/2}$ 35.3 eV), and oxide (W $4f_{7/2}$ 36.2 eV; W $4f_{5/2}$ 37.9 eV) [18]. These data suggest that, on the catalyst surface, more than 65% of the tungsten is in the sulfide form,



Fig. 1. Dependence of the naphthalene conversion on the W content in the feedstock. Reaction conditions: $T = 350^{\circ}$ C, $P_{H2} = 5.0$ MPa, and t = 5 h.

while about 30% of the tungsten is in the oxygen environment.

The nickel present on the catalyst surface is also in both the sulfide and oxygen environment. The deconvolution of the Ni 2p level has shown that the nickel is in three states: the NiS sulfide (Ni2p, 852.5 eV; Ni2p_{1/2} 869.5 eV), the Ni–W–S phase (Ni2p_{3/2} 853.6 eV; Ni2p_{1/2} 870.9 eV), and the NiO oxide (Ni2p_{3/2} 856.0 eV; Ni2p_{1/2} 873.8 eV) [18]. Seventy percent of the nickel is in the sulfide environment; as low as about 2% of the nickel is the form of pure NiS sulfide, while more than 65% of the nickel is included in the Ni–W–S complex sulfide, where the Ni atoms are in the environment of tungsten atoms.

The deconvolution of the S2p level has shown that the sulfur is in three states: S^{2-} (161.8 eV), oxysulfide (163.0 eV), and sulfate (168.7 eV) [18, 19]; in addition, the sulfur present on the catalyst surface is mostly in the form of oxysulfide (48%).

Catalytic Properties

The properties of the synthesized Ni–W–S catalyst were studied in a batch reactor at a temperature of 350° C and a hydrogen pressure of 5.0 MPa using 10% solutions of bicyclic aromatic HCs in benzene as model systems.

It has been shown that the naphthalene conversion increases with increasing tungsten content; at a tungsten content of 2500 ppm, the naphthalene conversion achieves 100%. The product is tetralin. A small amount of decalins (*cis-* and *trans-*stereoisomers) is formed at a tungsten content in the feedstock of 2500 ppm, yet no more than 5%. The ratio between *cis-* and *trans-*decalins is 1 : 1.1.



Fig. 2. Dependence of the SCA on the W : Ni molar ratio. Reaction conditions: $T = 350^{\circ}$ C; $P_{H2} = 5.0$ MPa; t = 5 h; and W content in feedstock, 680 ppm.

The dependence of the naphthalene conversion on the reaction time was studied at a 680-ppm tungsten content in the feedstock. As the reaction time increases, the naphthalene conversion increases and reaches 96% within 7.5 h. Accumulation of decalins is observed after 7.5 h; after 10 h, the decalin content is 32% and the ratio between *cis*- and *trans*-decalins is 1:1.7.

The addition of nickel (oil-soluble salt nickel(II) 2-ethylhexanoate) has a positive effect on the activity of the resulting catalyst. Even the addition of a small amount of nickel (W : Ni molar ratio, 3:1; W content, 680 ppm; reaction time, 5 h) leads to an increase in the naphthalene conversion from 62 to 88%. In addition, the two stereoisomeric forms of decalin were identified in the products; the amount of the stereoisomers is about 7%; the ratio between *cis*- and *trans*-decalins is 1:2.5.

With a further increase in the nickel content of the HC feedstock, the naphthalene conversion became 96–99%; therefore, the catalytic activities of the resulting systems were compared in terms of SCA, which takes account of both the naphthalene conversion and the product selectivity (Fig. 2).

At a molar ratio of W : Ni = 1 : 2, the naphthalene conversion is 99% to form 76% tetralin and 24% decalin with a *cis*- to *trans*-decalin ratio of 1 : 1.6. An increase in the nickel(II) salt concentration leads to a decrease in SCA: even at a W : Ni molar ratio of 1 : 3, the conversion decreases to 96% and the decalin selectivity is no more than 20%, while the ratio between *cis*-and *trans*-decalins remains unchanged (1 : 1.6).

As the nickel content in the feedstock is increased to 1350 ppm (at a W: Ni molar ratio of 1: 2), the naphthalene conversion makes 99% within 2.5 h to form 88% tetralin and 12% decalin. An increase in the reaction time leads to an increase in the decalin content in the system; by 10 h, decalins are the main reaction

Anomatia anonaund	Selec	Conversion 0		
Aromatic compound	decalins	tetralins		
1-Methylnaphthalene	87	13	100	
2-Methylnaphthalene	92	8	99	
2,3-Dimethylnaphthalene	40	60	99	
2,6-Dimethylnaphthalene	60	40	93	
1,5-Dimethylnaphthalene	66	34	100	
1,8-Dimethylnaphthalene	59	41	99	
2,7-Dimethylnaphthalene	62	38	100	
2,3,6-Trimethylnaphthalene	55	45	100	

Table 1. Hydrogenation of methylnaphthalenes. Reaction conditions: W content, 1350 ppm; W : Ni = 1 : 2; t = 10 h; $T = 350^{\circ}$ C; and $P_{H_2} = 5$ MPa

products with a *trans*-decalin selectivity of 72%. An increase in the reaction time also results in a change in the ratio between *cis*- and *trans*-decalins from 1:1.3 to 1:2.6 (reaction time of 2.5 and 10 h, respectively). This effect can be due to the fact that *trans*-decalin is the thermodynamically favored stereoisomer of decalin.

It has been shown that the resulting catalyst is active in the hydrogenation of naphthalenes with one, two, and three methyl substituents (Table 1).

The hydrogenation of bicyclic aromatic HCs bearing one methyl substituent was studied using 1-methylnaphthalene and 2-methylnaphthalene as an example. In the hydrogenation of monomethylated naphthalenes, the main products are methyldecalins. In the hydrogenation of 1-methylnaphthalene, the methyldecalin selectivity is 87%; in this case, both 1-methyldecalins and 2-methyldecalins are formed; the formation of the latter is caused by the migration of the alkyl substituent. The two compounds are formed as four stereoisomers (trans-anti-, trans-syn-, cis-anti-, and cis-syn-methyldecalins). The total amount of 2-methyldecalins in the reaction products is 19%; the main 2-methyldecalin stereoisomer is trans-syn-2-methyldecalin (7%). The main end product of the hydrogenation of 1-methylnaphthalene is *trans-anti-1-meth*vldecalin (the most thermodynamically stable 1-methyldecalin [20]); the selectivity for this product is 35%. The *cis*- to *trans*-methyldecalin ratio is 1 : 2.6.

The amount of methyltetralins remaining in the system does not exceed 13%. The hydrogenation rate of the unsubstituted ring is several times higher than that of the ring with an alkyl substituent; thus, the main methyltetralin isomer produced during the hydrogenation of 1-methylnaphthalene is 5-methyltetralin; the amount of this material in the total content of methyltetralins is 50%. This fact is attributed to the presence of steric hindrances to the adsorption of methylnaphthalene by the substituted aromatic ring on the catalyst surface [20]. It should also be noted that in addition to the hydrogenation of aromatic

rings, the migration of the alkyl substituent occurs, as evidenced by published data [21]. Thus, in addition to 5-methyltetralin and 1-methyltetralin, the hydrogenation of 1-methylnaphthalene led to the formation of 2-methyltetralin and 6-methyltetralin; however, the amount of these products in the total methyltetralin content does not exceed 4%.

In the hydrogenation of 2-methylnaphthalene, the methyldecalin selectivity is 92%. As in the case of hydrogenation of 1-methylnaphthalene, four stereoisomers of both 2-methyldecalin and 1-methyldecalin are formed in the hydrogenation of 2-methylnaphthalene. The total amount of 1-methyldecalins in the reaction products is 17%; the main 1-methyldecalin is trans-syn-1-methyldecalin (11%). The main end product of the hydrogenation of 2-methylnaphthalene is trans-syn-2-methyldecalin (the most thermodynamically stable stereoisomer of 2-methyldecalin [20]); the selectivity for this product is 44%. The ratio between cis- and trans-methyldecalins in the hydrogenation of 2-methylnaphthalene significantly differs from the ratios between cis- and trans-decalins in the hydrogenation of naphthalene or 1-methylnaphthalene: it is 1 : 6.

In the hydrogenation of 2-methylnaphthalene, the amount of methyltetralins remaining in the system does not exceed 8%. The main methyltetralin isomer formed during the hydrogenation of 2-methylnaph-thalene is 6-methyltetralin; the amount of this product in total methyltetralins is 49%. It should also be noted that the migration of the alkyl substituent is more active than in the case of hydrogenation of 1-methyl-naphthalene. Thus, in addition to the formation of 6-methyltetralin and 2-methyltetralin, the formation of 5-methyltetralin and 1-methyltetralin was observed in the hydrogenation of 2-methylnaphthalene; the amount of these products in total methyltetralins is more than 20%.

In a 10-h reaction, the conversion of all these dimethylated naphthalenes is 93–100%. In [22] we noted that dimethylnaphthalenes can be conditionally

Sulfiding agent	Calvert	Selecti	Naphthalene		
Sumaing agent	Solvent	decalins	tetralins	conversion, %	
Elemental sulfur	Benzene	24	76	99	
DMDS	Benzene	24	76	100	
DMSO	Benzene	20	80	100	
DMDS + DMSO	Benzene	14	86	100	
DMDS	<i>n</i> -Hexadecane	45	55	98	
DMSO	<i>n</i> -Hexadecane	30	70	13	
DMDS + DMSO	<i>n</i> -Hexadecane	12	88	92	

Table 2. Effect of the sulfiding agent on the catalyst activity in the hydrogenation of naphthalene. Reaction conditions: $T = 350^{\circ}$ C; $P_{H_{2}} = 5.0$ MPa; t = 5 h; W content, 680 ppm; W : Ni = 1 : 2; and S content, 25000 ppm

divided into two groups depending on the number of isomeric forms of the product dimethyltetralin. The hydrogenation of 1,8-dimethylnaphthalene, 2,6-dimethylnaphthalene, 1,5-dimethylnaphthalene, and 2,7dimethylnaphthalene results in the formation of a single appropriate form of dimethyltetralin owing to the symmetric arrangement of the methyl substituents on different aromatic rings. In the hydrogenation of these dimethylnaphthalenes, the main products are dimethyldecalins in different stereoisomeric forms.

The hydrogenation of 2,3-dimethylnaphthalene results in the formation of three isomeric forms of dimethyltetralin: 6,7-dimethyltetralin, 2,3-transdimethyltetralin, and 2,3-cis-dimethyltetralin because the methyl substituents in this dimethylnaphthalene are arranged on one aromatic ring. It should be noted that the main form of the resulting dimethyltetralin will be dimethyltetralin bearing substituents in the 6- and 7-positions owing to the fact that the unsubstituted aromatic ring undergoes hydrogenation more readily. In this case, the selectivity of hydrogenation for dimethyldecalins (40%) is lower than that of the other discussed substrates; this feature can be attributed to steric hindrances created by the dimethylated aromatic ring to the adsorption of 6,7-dimethyltetralin on the catalyst surface.

It is noteworthy that as in the case of hydrogenation of monomethylnaphthalenes, in addition to the hydrogenation of the aromatic rings, both the migration of the methyl substituents the formation of dealkylation products occurred to a small extent.

The 2,3,6-trimethylnaphthalene conversion is 100% and results in the formation of 2,6,7-trimethyltetralin, 2,3,6-*trans*-trimethyltetralin, 2,3,6-*cis*-trimethyltetralin, about 1% other trimethyltetralins due to the migration of the methyl groups, and a small amount of dealkylation products. The main trimethyltetralin isomer is 2,6,7-trimethyltetralin (selectivity of 26%); the selectivity for 2,3,6-*cis*-trimethyltetralin and 2,3,6-*trans*-trimethyltetralin is 2 and 15%, respectively. In the hydrogenation of 2,3,6-trimethylnaphthalene, the trimethyldecalin selectivity is 55%, which is slightly lower than that in the hydrogenation of mono- and dimethylated naphthalenes; this difference can also be due to the steric hindrances created by the trimethylated aromatic ring to the adsorption of 2,6,7-trimethyltetralin on the catalyst surface.

Selection of Sulfiding Agent

In addition to elemental sulfur, dimethyl disulfide (DMDS) and dimethyl sulfoxide (DMSO) were tested as a sulfiding agent. In the case of using a DMDS–DMSO mixture as a sulfiding agent, the DMDS : DMSO ratio was 1:2. When a 10% naphthalene solution in benzene was used as a model feedstock, all of these sulfiding agents were soluble in the HC feedstock. The naphthalene conversion was 99–100% in all cases (Table 2). The main product was tetralin. The lowest decalin yield (14%) was observed in the case of a DMDS–DMSO mixture. The ratio between *cis*- to *trans*-decalin remained almost unchanged, being at the level of 1:2 to 1:2.5 for all the sulfiding agents.

In the case of using a 10% naphthalene solution in *n*-hexadecane as a model feedstock, a significant effect of the sulfiding agent on the catalytic activity of the resulting Ni–W–S particles was observed. Thus, the catalyst synthesized using DMSO, which is immiscible with *n*-hexadecane, as a sulfiding agent showed the lowest activity. The naphthalene conversion was as low as 13%. The highest catalytic activity was found for the catalyst prepared using the sulfiding agent DMDS, which is soluble in this feedstock. Thus, the naphthalene conversion was 98%; the decalin selectivity was 45%. This difference in the activity of the resulting catalysts can be attributed to the presence of oxygen in DMSO, which can lead to a slowdown in the sulfide formation. The us of the mixed DMDS-DMSO agent dramatically increased the activity of the catalyst system. This finding suggests that in order to increase the activity of the catalyst synthesized from DMSO solutions, it is necessary to use an additional sulfiding agent (DMDS). It is noteworthy that the ratio between cis- and trans-decalins remains

	LCO	Hydrofining products		
Characteristic		W content in feedstock, wt %		
		0.3	2.1	4.2
Sulfur, ppm	3320	99	99	98
Monocyclic aromatic HCs, wt %	34	57	40	29
Bicyclic aromatic HCs, wt %	27	7.5	2	2
Polycyclic aromatic HCs, wt %	5	0.5	0	0
Σ aromatic HCs, wt %	66	65	42	31

 Table 3. Characterization of light cycle oil and hydrofining products

unchanged at the level of 1:2 for all the sulfiding agents.

tion of monocyclic HCs contained in the feedstock occurs.

LCO Hydrofining

In this study, the possibility of applying the synthesized catalyst to the hydrofining of actual feedstock with a high concentration of sulfur and aromatic HCs has been explored using LCO as an example. Table 3 shows the data on the hydrodearomatization and hydrodesulfurization of LCO as a function of the weight fraction of the precursor in the feedstock.

The data show that the hydrodesulfurization of LCO under these experimental conditions can result in the formation of the hydrofining product with a total sulfur content of 0.01%. The degree of hydrodes-ulfurization is 97% and does not change with increasing precursor content in the feedstock.

The features of the hydrodearomatization of LCO hydrocarbons are similar to those of the hydrogenation of the model systems. The total aromatics content of the hydrofining products decreases with the increasing precursor content in the feedstock. The amount of biand polycyclic aromatic HCs significantly decreases; at a W content in the feedstock of 2.1 wt %, the amount of bicyclic polyaromatic HCs in the hydrofining product is no more than 2%, while polycyclic aromatic HCs are not identified at all. The hydrogenation of aromatic HCs having two and more aromatic rings leads to the formation of not only naphthenic HCs, but also monocyclic aromatic HCs, as was shown for the model systems. Thus, at a W content in the feedstock of 0.3 and 2.1 wt %, the content of monocyclic aromatic HCs in the hydrogenation products is higher than that in the original LCO. However, with an increase in the tungsten content in the feedstock, the amount of monocyclic aromatic HCs decreases; this fact indicates the occurrence of the hydrogenation of monocyclic aromatic HCs produced during the hydrodearomatization of bi- and polycyclic aromatic HCs; at a W content in the feedstock of 4.2 wt %, the amount of monocyclic aromatic HCs becomes lower than that in the feed LCO, thereby suggesting that not only the deep hydrogenation of bi- and polycyclic HCs directly to naphthenic HCs, but also the hydrogena-

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CONCLUSIONS

Thus, a nickel-tungsten sulfide catalyst has been first prepared by the in situ decomposition of the oilsoluble tungsten hexacarbonyl precursor in a hydrocarbon feedstock using the oil-soluble salt nickel(II) 2-ethylhexanoate as a source of nickel. It has been revealed that the optimum W : Ni molar ratio is 1 : 2. It has been shown that the synthesized catalyst exhibits high activity in the hydrogenation of bicyclic HCs and can be used in the hydrofining of a feedstock with high sulfur and aromatics content, as evidenced by the example of LCO.

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