International Journal of Technology

Modified Polymetallic Zeolite-Based Catalysts for Hydroprocessing Diesel Oil Fraction and Tetradecane

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Abstract. According to international standards, motor fuels require limits on the content of sulfur, benzene, aromatic and olefinic hydrocarbons. Achieving these standards requires the development of new, active, and selective catalysts alongside advancement in technologies for deep hydrotreating and hydroprocessing. Therefore, this study aimed to investigate tetradecane and diesel oil fraction hydroprocessing using modified zeolite-based Ni(Co)-Mo(W)/Al$_2$O$_3$-ZSM-5 catalysts under varying processing conditions. The novelty is attributed to the synthesis of new catalysts based on ZSM-5 type zeolite, modified with metals Ni(Co)-Mo(W) and active additives of rare earth metals and phosphorus. The results showed that after hydrotreating diesel oil fraction on KT-3 catalyst, the pour point and sulfur level decreased from -27 to -57°C and 0.141 to 0.059% respectively, while the yield of the liquid phase was 92.2%. The lowest residual sulfur content (0.005%) was observed on KT-4 catalyst at 400°C. Based on electron microscopic examinations, modified zeolite-based catalysts were distributed in a highly dispersed manner, and the metal components in the active phase were primarily in the oxidized state, generating associate clusters on the surface. The dispersion, structure, and state were influenced by the characteristics of catalyst components. In conclusion, modified zeolite-based catalysts had multifunctional properties, facilitating hydrocracking, hydroisomerization, hydrodesulfurization, and dehydrogenation reactions concurrently.

Keywords: Catalyst; Diesel fraction; Hydroprocessing; Motor fuel; Tetradecane

1. Introduction

The efficient use of petroleum feedstock is potentially achieved by catalytic processing of hydrocarbons into practical important products. In this context, a key source of energy is diesel fuel, which is economical, environmentally friendly, practical, and generally effective in many industrial processes requiring large amounts of energy. Diesel engines are capable of providing stable and reliable power for a variety of industrial applications.

The growing trend of performance requirements for motor fuel underscores the need to develop new technological and environmental solutions for oil refining. This fuel is the main component of plastics, synthetic fibers, resins, rubbers, dyes, surfactants, and pharmaceutical products.

Hydrotreating stage in petroleum raw material processing ensures the production of clean motor fuel that meets environmental standards. Further intensification of production relies on developing new, more active, and selective catalysts. In this context, an important and topical issue is the formation of efficient catalytic systems for hydroprocesses. Zeolite catalysts, particularly when based on highly silica zeolite of the pentasil family, are a promising material in the petrochemical and oil refining industry (Suhartono *et al.,* 2023). These catalysts are widely used due to the unique microporous structure and acid-base properties, which enable the conversion of light alkanes into valuable products during petrochemical synthesis (Zhang *et al.,* 2023).

Various studies have synthesized hydrocracking catalysts with different zeolites to investigate the role of modified zeolite-Y in crude oil hydroconversion (Ding *et al.*, 2021). The results showed that catalysts with high acidity, strong acid sites, and mesopores could improve crude oil conversion.

A previous study (Huseynova *et al.,* 2022) provided an overview of zeolite-based catalysts used in the alkylation of benzene and toluene with olefins, isobutane, and butenes with butane-butene fractions, gasoline and oil fractions with olefins, as well as propane-propylene and butane-butylene fractions of catalytic cracking. Developing novel technologies in this field requires a new generation of catalysts for the processing of hydrocarbon raw materials. International standards mandate that motor fuel contains a significant amount of sulfur, benzene, aromatic hydrocarbons, and olefin hydrocarbons.

Catalytic hydroprocessing of sulfurous and paraffinic oils, comprising hydrotreatment, hydroisomerization, and hydrogenation, achieves a high degree of quality for commercial products. Hydrodesulfurization, a chemical change that removes sulfur from gas and refined crude products such as gasoline, jet fuel, kerosene, alongside diesel and fuel, upgrades the octane number of the resolvent streams (Sikkander *et al.,* 2022).

A study by (Majodina *et al.,* 2023) compared traditional hydroprocessing and recently improved catalysts, detailing the chemical considerations underlying the selection of mineral materials used in both. Furthermore, investigations into the electronic interactions of more economical and abundant metals including Nb, V, and Fe with other elements and supporting materials have led to a better understanding of the synergistic effects that help access noble metal-like properties.

To increase the production of petroleum products, expand the range, and improve quality, it is necessary to change the existing oil refining technology using highly efficient catalysts. A highly promising CoMo catalyst for hydrotreating low-pressure diesel fuel on carriers made of thermally activated aluminum hydroxide was investigated in comparison with a commonly imported analog (Salnikov *et al.*, 2023). Previous studies also developed technologies suitable for processing rehydrated pseudoboehmites from flash-calcined aluminum hydroxide to prepare catalysts for hydrotreating light and heavy oil fractions (Bayanov *et al.,* 2023). Modification with metals enhances catalyst acidity, improving catalytic performance, conversion, and selectivity/yield toward the product (Mavai, 2022). To advance the field of study, new multifunctional catalysts are needed to effectively hydrotreat diesel fractions in a single stage. This entails removing sulfur-containing compounds, hydrogenating unsaturated and aromatic compounds, hydroisomerization, and selective hydrocracking of n-paraffin hydrocarbons (Tuktin *et al.*, 2021).

The development of new and highly efficient catalysts for hydroimprovement of diesel fractions is crucial (Janardhan, Shanbhag and Halgeri, 2014; Zhang *et al.,* 2010; Saih and Segawa, 2009; Rodrıguez-Castellon, Jimenez-Lopez, and Eliche-Quesada, 2008). A previous study (Fitri *et al.,* 2022) used citronella oil as a dietary supplement to diesel fuel. Citronella fractions and oil have shown great potential as bio-additives to diesel fuel, evidenced by

acceptable density and viscosity in tested various concentrations (0.1 - 0.5%). Co-Ni/HZSM-5 catalyst with a hierarchical porous structure was tested for hydrocracking of vegetable oils at a temperature of 400°C, and a pressure of 20 bar for 2 hours. The liquid product had similar hydrocarbon compounds to petroleum diesel fuel, with the most common being pentadecane and heptadecane (Marlinda *et al.*, 2022).

The influence of technological regimes on the yield and hydrocarbon composition of products formed during the cracking of commercial and M-100 fuel oil in the presence of air in the reactor was studied by (Shakiyeva *et al.,* 2022). Natural Taizhuzgen zeolite and Narynkol clay were used to prepare catalysts.

Sulfide catalysts were reportedly obtained through mechanochemical combination of commercial powders including molybdenum, cobalt, and nickel (Fedushchak *et al.*, 2019). The study discussed the activity of catalysts in model hydrodesulfurization reactions of dibenzothiophene and 4,6-dimethyldibenzothiophene as well as in hydrotreating S-components of diesel fraction. Based on previous reports, the higher activity of Ni-based catalysts is due to the superior hydrogenizing capacity. Studies by (Altynov *et al.*, 2023; Aleksandrov, Buhtiyarova and Reshetnikov, 2019) examined the behavior of CoMo/Al$_2$O$_3$ catalyst in hydrotreating a straight-run diesel fraction with a high sulfur content (more than 2 wt.%) mixed with light gas oil in the temperature range of 335 - 365°C at a volumetric feed rate of 0.8 - 2.5 h^{-1}. Adding gas oil to the straight-run diesel fraction during hydrotreating has diverse effects based on the temperature and feed rate of the raw materials (Tanimu *et al.*, 2022).

A study examined catalytic abilities of trimetallic NiMoWS catalysts supported on aluminum oxide during hydrotreating of straight-run diesel fraction (Nikul'shina *et al.*, 2019). The results showed that the oxide precursor's nature had a significant effect on catalytic activity. Mixing n-heptane, n-dodecane, tetralin, and decalin with diesel fuel linearly changes density, viscosity and improves atomization (Wei *et al.*, 2022). The study by (Jaroszewska *et al.*, 2021) showed that catalysts containing titanium (HTiMCM-41 and NiMo/HTiMCM-41) improved textural properties, as well as acidity and binding energy with the metal substrate than Al-based analogs (HAlMCM -41 and NiMo/HAlMCM-41). Replacing aluminum or titanium in modifying MCM-41 zeolite significantly affects the properties and activity of Ni catalysts.

Typical transition metal sulfides Ni/Co-promoted Mo, as well as W-based bi- and tri-metallic catalysts, are used for selective removal of sulfur from refractory compounds. The review (Prihadiyono *et al.*, 2022; Leon *et al.*, 2019) examined three very specific topics of catalysts to produce ultra-low sulfur diesel. Furthermore, (Winarto *et al.*, 2024) explored a biphasic hydrogenation approach using solid NR dissolved in a solvent and a hydrogen source (hydrazine hydrate and hydrogen peroxide) mixed in water. The choice of solvents, catalysts, and the water-to-solvent volume ratio were examined for the impact on hydrogenation.

Studies on developing effective catalysts and technologies to process diesel fractions into valuable chemical products and motor fuel are crucial (Laredo *et al.,* 2020; Kar, Göksu and Yalman, 2018). The production of high-quality commercial petroleum products can be achieved using catalysts prepared based on aluminosilicates with a zeolite structure of the ZSM-5 type for hydrorefining diesel oil fractions (Tuktin *et al.*, 2022).

The objective of this study was to analyze hydroprocessing of tetradecane and diesel oil fraction on modified zeolite-based Ni(Co)-Mo(W)/Al$_2$O$_3$-ZSM-5 catalysts. Tetradecane, an alkane component of diesel oil fraction was used as a model hydrocarbon. Improving the properties of diesel fraction is considered one of the most important processes in the petrochemical industry, leading to the investigation in laboratory studies based on

hydroisomerization of n-hexadecane as the main model reaction (Aljajan *et al.*, 2023). Zeolite-based bifunctional catalysts have proven effective due to significant acidity, shape selectivity, and relative resistance to deactivation.

This study examined the impact of catalyst components and processing conditions on the conversion of raw materials and the main characteristics of the upgraded diesel fuel. For the first time, modified catalysts based on zeolite of ZSM-5 structural type were obtained. The introduction of modifying additives into the zeolite led to an increase in the concentration of weak acid sites and the yield of liquid catalyst in hydroprocessing of tetradecane and diesel oil fraction.

2. Materials and Methods

This study investigated hydroprocessing of tetradecane and diesel oil fraction oil on zeolite catalysts modified using metals of variable valence. A series of new catalysts with matrix structure Ni(Co)-Mo(W)/Al_2O_3-ZSM-5 were synthesized as shown in Table 1.

Table 1 Composition of the developed catalysts

No.	Catalyst sample	Catalyst components
1	KT-1	CoO-MoO_3-P_2O_5-La_2O_3/Al_2O_3-ZSM-5
2	KT-2	CoO-WO_3-P_2O_5-La_2O_3/Al_2O_3-ZSM-5
3	KT-3	NiO-MoO_3-P_2O_5-La_2O_3/Al_2O_3-ZSM-5
4	KT-4	CoO-NiO-MoO_3-P_2O_5-La_2O_3/Al_2O_3-ZSM-5

The synthesis of modified zeolite-based catalysts was performed by saturating a mixture of peptized aluminum hydroxide and zeolite ZSM-5 (China) with aqueous solutions of metal salts. These include $(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$ (Cherkasy chemical reagents plant, Russia), $Ni(NO_3)_2 \cdot 6H_2O$ (Ural Chemical Plant, Russia), $Co(NO_3)_3 \cdot 6H_2O$ (Novosibirsk Rare Metals Plant, Russia), $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (Cherkasy chemical reagents plant, Russia), $La(NO_3)_3 \cdot 6H_2O$ (Novosibirsk Rare Metals Plant, Russia) and modifying additives. After molding, catalysts were dried at 150°C and calcined at 550°C for 5 hours. Before the experiments, catalysts were subjected to preliminarily sulphidation to increase activity in the reactor. The synthesized catalysts were tested through hydroprocessing tetradecane and diesel oil fraction using flow-through installation (Figure 1) with a stationary catalyst bed. The testing conditions included temperature ranging from 320-400°C, hydrogen pressure of 4.0 MPa, and a volumetric feed rate of 2 h^{-1}.

Hydrocarbon composition of reaction products was analyzed using Khromatek-Kristall and Khromatek-Kristall 5000 chromatographs (Russia). The chromatograph calculates the fractional composition automatically. For the analysis of hydrocarbons, a glass column 3 m long, 4 mm in diameter, filled with γ-Al_2O_3 was used. The integral selectivity (S) of aromatization, dehydrogenation, and cracking was calculated using the formula $S = Y/X$, where Y is the yield of products; and X is the feedstock degree of conversion.

The analysis of sulfur content, pour point, as well as cloud point of diesel oil fraction and products of hydroprocessing was carried out at Oilsert International LLP (Almaty, Kazakhstan). Various methods were used to analyze the physical and chemical characteristics of the developed catalysts. Surface area and porosity were measured by BET method on an AccuSorb unit manufactured by Micromeritics (USA), while electron microscopy was performed using an EM-125K transmission electron microscope (Williams and Carter, 2009). Microdiffraction images were interpreted using standard ASTM tables. To examine the number of acid sites and their strength distribution, the method of temperature-programmed desorption of ammonia was used (Mustafayeva, 2012).
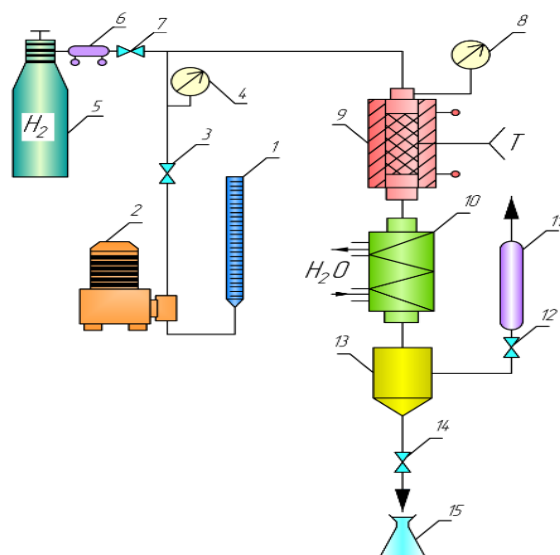
Figure 1 Scheme of a laboratory installation of hydroprocessing, where 1 – burette, 2 – pump; 3, 7, 12, 14 – valves; 4, 8 – pressure gauges; 5 – hydrogen cylinder; 6 – reducer; 9 – reactor; 10 – refrigerator; 11 – rotameter; 13 – separator; 15 – flask

3.   Results and Discussion

The development of new catalysts effective for processing low-solidification diesel oil fractions into high-octane products is currently a major concern. The original diesel oil fraction has the following characteristics: pour point -27°C, cloud point -18°C, and a high content of n-alkanes, which solidifies at higher temperatures compared to branched analogs. In addition, the sulfur content is approximately 0.141%.

Tetradecane, an n-alkane, and a component of diesel oil fraction was used as a hydrocarbon model. The conversion of tetradecane on the developed modified zeolite-based catalysts was studied by varying the technological parameters of the process.

During hydroprocessing of n-tetradecane on KT-1 catalyst (Figure 2), the liquid catalysate formed n-alkanes, isoalkanes, olefins, aromatic hydrocarbons, and naphthenes. With an increase in temperature from 320 to 400°C, the degree of conversion increased from 41.2 to 74.5%. The yield of the liquid phase decreased from 92.3 to 54.1% with an increase in temperature. In addition, the yield of isoalkanes and aromatic hydrocarbons on KT-1 catalyst increased from 12.9 to 22.3% and 5.5 to 18.3%, respectively. Based on the results, the content of olefins and naphthenic hydrocarbons varied insignificantly.

On KT-2 catalyst, hydroprocessing of tetradecane led to an increased content of isoalkanes, rising from 15.0 to 35.3% as the temperature rose from 320 to 400°C, while the amount of aromatic hydrocarbons decreased from 5.1% to 6.3%. During hydroprocessing of tetradecane on synthesized catalysts, the highest yield of isoalkanes was observed on KT-3 catalyst at 400°C. Based on the results, a sharp rise was observed in the yield of isoalkanes from 17.1 to 37.7% with an increase in temperature.

Compared to other catalysts, KT-4 produced a smaller quantity of olefinic hydrocarbons as reaction products. A rise in the temperature from 320 to 400°C led to a change in the conversion from 38.8 to 83.4%. Under these conditions, isoalkanes and aromatic hydrocarbons increased from 13.4 to 30.5% and 6.2 to 19.2%, respectively, while the naphthenes content decreased from 3.0 to 2.3%.

For all catalysts studied, the degree of tetradecane conversion increased with rising reaction temperature. Based on the results, the developed modified zeolite-based catalysts

showed polyfunctional properties, simultaneously facilitating isomerization of n-alkanes, dehydrogenation, and dehydrocyclization.
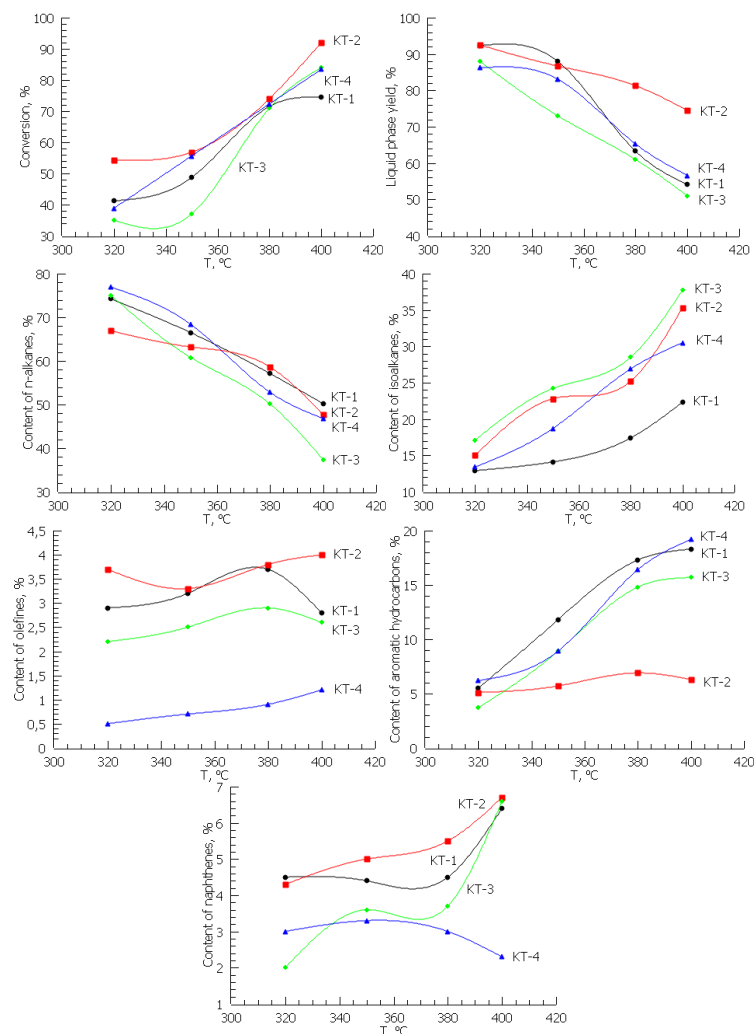

Figure 2 Results and composition of tetradecane hydroprocessing products using catalysts CoO-MoO$_3$-P$_2$O$_5$-La$_2$O$_3$/Al$_2$O$_3$-ZSM-5 (KT-1), CoO-WO$_3$-P$_2$O$_5$-La$_2$O$_3$/Al$_2$O$_3$-ZSM-5 (KT-2), NiO-MoO$_3$-P$_2$O$_5$-La$_2$O$_3$/Al$_2$O$_3$-ZSM-5 (KT-3) and CoO-NiO-MoO$_3$-P$_2$O$_5$-La$_2$O$_3$/Al$_2$O$_3$-ZSM-5 (KT-4)

Catalysts were evaluated during hydroprocessing of diesel oil fraction (Figure 3). At a temperature of 400°C, the lowest sulfur content (0.005%) was observed on KT-4 catalyst. The pour point of diesel oil fraction decreased by 15 - 30°C compared to the feedstock after hydroprocessing on the developed catalysts. KT-3 catalyst produced the most significant drop in pour point. After hydroprocessing of diesel fraction at 400°C, the pour point dropped to -57°C, and the yield of the liquid phase was 92.2%.

During hydroprocessing of diesel fraction on the developed catalysts, simultaneous reactions of hydroisomerization, hydrotreatment, and hydrocracking were observed. For example, after hydroprocessing of diesel oil fraction on KT-3 catalyst at 400°C, the sulfur content decreased from 0.141 to 0.059%, and the pour point reduced from -27 to -57°C. On KT-4 catalyst at 400°C, the reduction reached 0.005% and -55°C respectively.

Catalyst activity is influenced by surface structure, composition, and state of active sites. Different methods can be used to investigate the physicochemical traits of catalysts including BET, temperature-programmed desorption of ammonia, and electron microscopy.
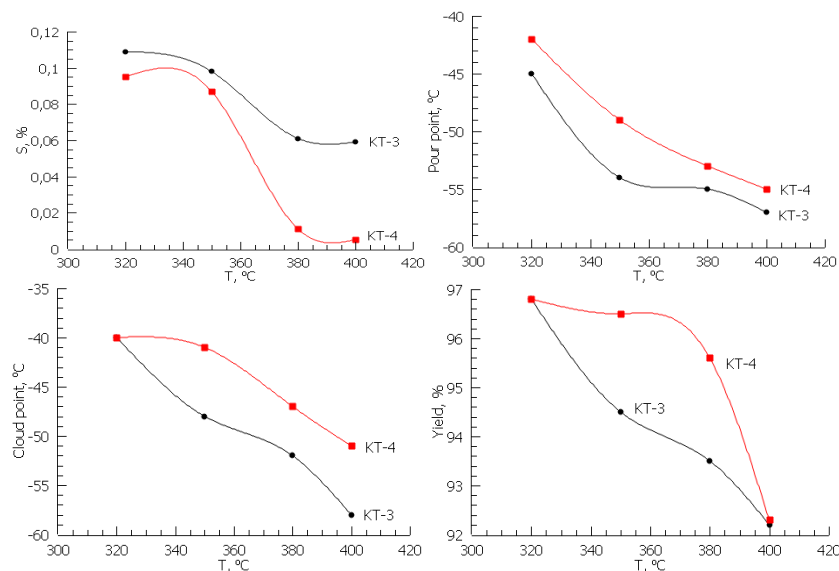
Figure 3 Results of diesel oil fraction hydroprocessing on KT-3 and KT-4 catalysts

BET analysis showed that the surface area of the developed catalysts ranged from 221.0-285.0 m^2/g and the pore diameter was between 1.5-3.5 nm. Furthermore, the acid-base characteristics of catalysts are essential for hydrocarbon processing process. In a previous study (Wei *et al.,* 2020), Ni-Mo catalysts supported on Ni-modified ZSM-5 zeolites prepared by co-impregnation method showed higher stability and isomerization selectivity in n-octane hydroconversion. This enhanced property was attributed to the synergistic effect between Brønsted acid sites and Lewis acid sites on catalysts. The acid-base properties of catalysts were determined through temperature-programmed desorption of ammonia (Table 2).

Table 2 Acid-base properties of catalysts

Catalyst	Desorption temperature, ^0C	Desorbed NH_3, 10^{-4} mole/g catalyst
KT-1	195	23.4
KT-2	185	28.0
KT-3	220	32.5
KT-4	225	29.6

The data showed that acid centers with a desorption temperature of 195°C predominated on the surface of KT-1 catalyst, with a concentration of $23.4 \cdot 10^{-4}$ mole/g. The amount of ammonia desorbed from the surface of КТ-2 catalyst was $28.0 \cdot 10^{-4}$ mole/g and the concentration of acid sites on КТ-3 catalyst was $32.5 \cdot 10^{-4}$ mole/g. On the surface of KT-4 catalyst, ammonia was adsorbed in two forms with T_{max} equal to 185 and 225°C. KT-3 catalyst, characterized by the highest concentration of acid sites ($32.5 \cdot 10^{-4}$ mole/g) and an average binding energy corresponding to desorption temperature of 220°C, demonstrated high hydroisomerization activity in hydroprocessing of tetradecane and diesel oil fraction. Metals with different degrees of oxidation can be found in the composition of acid sites, attached both inside and on the outer surface of the zeolite cavities, ensuring the multifunctionality of catalytic system.

Catalyst activity is influenced by the surface structure, phase composition, and the state of modifying additives. In the study by (Abdullaev *et al.,* 2021), the surface of SSZ-13 zeolite was modified with varying amounts (1-15%) of tungsten oxide, demonstrating significantly improved selectivity and yield of propylene from ethylene. This enhancement was attributed not only to softer and reduced strong acid sites but also to limited diffusion of

bulky products, as confirmed by scanning transmission electron microscopy and energy-dispersive X-ray spectroscopy (STEM-EDS) data. An electron microscopy study was carried out to examine the structure and state of active centers in catalysts promoted by Co, Ni, Mo, and W, among others.

Electron microscopic studies showed that on the surface of KT-1 catalyst (Figure 4a), extensive accumulations of small particles were observed with diameter 3.0 - 5.0 nm, corresponding to a mixture of $MoOPO_4$, La_2O_3, MoO_5, and La_2MoO_3 phases. Small accumulations of highly dispersed particles with 8.0 - 10.0 nm in size were also found, which could be attributed to $La_4(P_2O_7)_3$. Furthermore, there were small transparent aggregates with d ≤ 20.0 nm related to $LaAlO_3$ in the γ-La° mixture. The emergence of γ-La° could be connected to redox processes occurring between the active phase components.
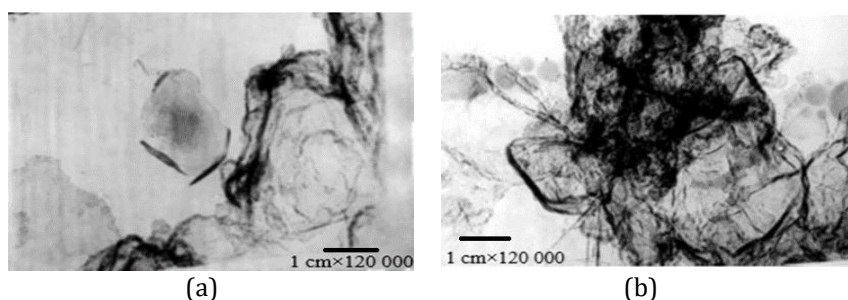

(a)   (b)

Figure 4 Electron microscopic images of CoO-MoO_3-P_2O_5-La_2O_3/Al_2O_3-ZSM-5 (KT-1) catalyst: (a) $MoOPO_4$, La_2O_3, MoO_5, and La_2MoO_3 phases (d = 3.0-5.0 nm); (b) $AlLa_3$, Co_2O_3, Co_2SiO_3, and La_6O_{11} formations (d = 4.0-6.0 nm)

The nature of the components in complex polymetallic catalysts for hydroprocessing of hydrocarbons has a significant effect on the dispersion and state of active centers. Formations with diameter 4.0 - 6.0 nm, consisting of $AlLa_3$, Co_2O_3, Co_2SiO_3, and La_6O_{11}, were prevalent on the surface of KT-1 catalyst (Figure 4b). Cobalt formed single structures of metallic Co° with a diameter of 2.5 nm on the surface. Additionally, there were accumulations (d ≈ 15.0 nm) of small particles (d ≈ 2.5 nm) consisting of $CoSi$, $CoSi_2$, and $MoPCo_2$; lamellar particles (d ≈ 15.0 nm) such as $MoPCo_2Si$, CoO, and Mo_3Si; semitransparent structures (d ≈ 2.5 nm) namely $MoO(OH)_2$, Co_2O_3, MoP_2, $Co_3Al_3Si_4$, and SiP_2O_7; alongside particles with d ≈ 6.0 - 10.0 nm, including LaP, MoO_3, and Mo_3Si. Accumulations containing $Co_2Mo_3O_8$, LaP_2O_7, $AlPO_4$, $CoOOH$, $MoOPO_4$, α-$Co(P_2O_7)$, and $La(MoO_4)_2$ had particles with different shapes in the range of 50-200 nm in diameter. In addition, there were particles 4-5 nm in size including $La_4(P_2O_7)_3$, $CoSi$, MoP, $MoSi_2$, La_6O_{11}, and $CoMoP_2$.

Highly dispersed structures of $AlNi$, Ni_2O_3, Mo_3O_5, and Mo_5Si_3 with d ≤ 2.0 nm were predominant on the surface of KT-3 catalyst (Figure 5). There were well-spaced small accumulations of $MoNiSi$, Ni_2O_3, $MoSi_2$, and M_6O_{11} particles with diameter 6.0 - 10.0 nm. In addition, the oxidized states of nickel Ni_2O_3 formed single islands, with a size ranging from 5.0 to 10.0 nm (Figure 5a). KT-3 catalyst was defined by clusters measuring 3.0 - 4.0 nm, formed by fine particles with d = 0.05 nm, containing $NiSi_2$ and Ni_2O_3. Particles with hexagonal faceting and diameters between 15.0 and 30.0 nm were also found, composed of $AlNi_2Si$, $AlNi$, La_2O_3, $MoO(OH)_2$, $AlMo_3$, $MoSi_2$, and Al_3La (Figure 5b). The discovered structures of $AlNi_2Si$, $AlMo_3$, $AlNi$, $MoSi_2$, and $LaAlO_3$ $NiSi_2$ indicated the incorporation of metal components from the active phase into the zeolite structure with the formation of new centers that could work as Lewis acid centers.

During hydroprocessing on polyfunctional catalysts with dehydrogenating, hydrogenating, and acidic abilities, n-alkane dehydrogenation occurs first on the metal

centers, and the olefin produced on the acid center is converted into a carbonium ion, which is easily isomerized (Tuktin *et al.,* 2019). $Mo_5O_7(OH)_2$, MoO_3, $NiMO_4$, $CoOOH$, $NiOOH$, $AlLa_3$, P and La, $MoNiP$, Ni_2O_3 particles with diameter ranging from 10.0 - 15.0 nm along the edge of dense and large aggregates were discovered on the surface of KT-4 catalyst (Figure 6a). Additionally, numerous loose formations of Mo_3O_5, Mo_5Si_3, Mo_6O_{11}, Al_3Ni, Ni_2O_3, and PLa_2 were observed with diameter of 3.0 - 5.0 nm. There were also clusters of $AlNi_2Si$ and Mo_3O_5 particles with diameters of 3.5 - 4.0 nm (Figure 6b).
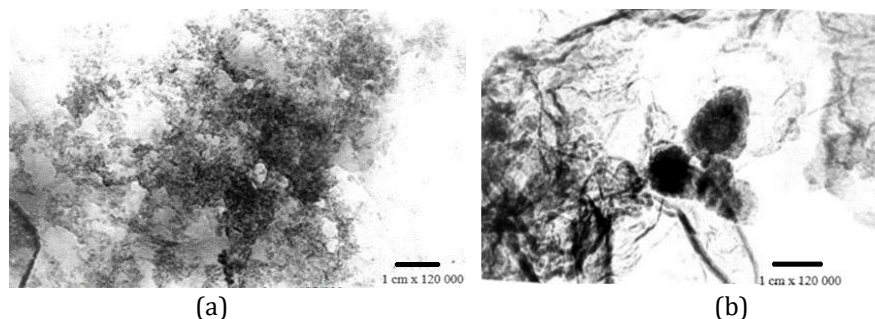

(a)   (b)

Figure 5 Electron microscopic images of $NiO-MoO_3-P_2O_5-La_2O_3/Al_2O_3$-ZSM-5 (KT-3) catalyst: (a) Ni_2O_3 structures (d = 5.0-10.0 nm); (b) $AlNi_2Si$, $AlNi$, La_2O_3, $MoO(OH)_2$, $AlMo_3$, $MoSi_2$, and Al_3La particles (d = 15.0-30.0 nm)

(a)   (b)
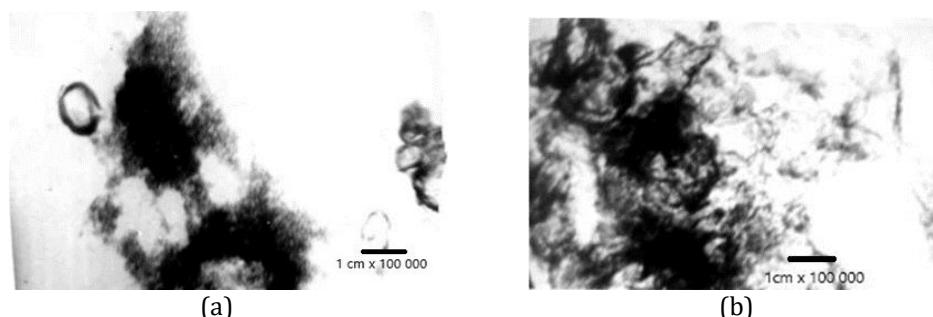
Figure 6 Electron microscopic images of $CoO-NiO-MoO_3-P_2O_5-La_2O_3/Al_2O_3$-ZSM-5 (KT-4) catalyst: $Mo_5O_7(OH)_2$, MoO_3, $NiMO_4$, $CoOOH$, $NiOOH$, $AlLa_3$, P and La, $MoNiP$, Ni_2O_3 particles (d = 10.0 - 15.0 nm); $AlNi_2Si$ and Mo_3O_5 particles (d = 3.5 - 4.0 nm)

Electron microscopy studies showed that particles on the surface of the developed catalysts were highly dispersed, with sizes ranging from 2.0 to 10.0 - 20.0 nm depending on the nature of the modifier metal and the amount of zeolite introduced. All the studied catalysts were characterized by the incorporation of modifier metals into the matrix structure with the formation of $CoSi$, $CoSi_2$, $MoPCo_2Si$, $Co_3Al_3Si_4$, Mo_3Si, Co_2Si, Mo_5Si_3, $AlNi$, $MoNiSi$, $MoSi_2$, $AlNi_2Si$, and $W(Si, Al)_2$. These structures can function as Lewis acid sites, while the phosphorus-containing centers including SiP_2, PLa_2, $MoNiP$, LaP, and Co_2P are also quite strong acidic centers. The modification of catalysts leads to the formation of highly dispersed heteronuclear clusters of complex composition, which are active in hydrotreatment and hydroisomerization reactions of diesel oil fraction (Gackowski *et al.,* 2020).

Studies have identified several types of surface structures found on the surface of these catalysts, differing significantly in size and chemical state of components. For instance, a small amount of hierarchical Y zeolite (10 %) mixed with alumina, nickel nitrate, and molybdenum oxide in the light diesel fuel hydrocracking catalyst, played a key role in selectively hydrogenating naphthalene and further ring-opening activity. The mesoporous structure of zeolite provided an effective interface and improved the accessibility of acid sites for bulk reagents (Zhang *et al.,* 2020). According to electron microscopy data, the

active phase catalyst components are mostly in the oxidized state, creating associate clusters on the surface. The dispersion, structure, and nature of the modifying additives in catalyst determine the active state.

4. Conclusions

In conclusion, this study evaluated hydroprocessing of tetradecane and diesel oil fraction using new modified zeolite-based Ni(Co)-Mo(W)/Al$_2$O$_3$-ZSM-5 catalysts under varying process conditions. The developed catalysts used in hydroprocessing diesel oil fraction showed polyfunctional properties, simultaneously facilitating hydrocracking, hydroisomerization, hydrodesulfurization, and dehydrogenation reactions. These results suggest that modification using metals with variable valence allows proper control of hydroisomerization, hydrodesulfurization, and hydrocracking activity of catalysts in hydroprocessing of diesel oil fraction, facilitating the production of fuel with low sulfur and pour point.

Acknowledgments

References

Abdullaev, M.U., Lee, S., Kim, T.-W., Kim, C.-U., 2021. Tungsten Oxide-Modified SSZ-13 Zeolite as an Efficient Catalyst for Ethylene-To-Propylene Reaction. *Catalysts*, Volume 11, p. 553

Aleksandrov, P.V., Buhtiyarova, G.A., Reshetnikov, S.I., 2019. Study of The Influence of Coker Gas Oil to The Straight-Run Gas Oil on The Process of Hydrotreating in The Presence of CoMo/Al$_2$O$_3$ catalyst. *Russian Journal of Applied Chemistry*, Volume 92, pp. 1077–1083

Aljajan, Y., Stytsenko, V., Rubtsova, M., Glotov, A., 2023. Hydroisomerization Catalysts for High-Quality Diesel Fuel Production. *Catalysts*, Volume 13, p. 1363

Altynov, A., Bogdanov, I., Lukyanov, D., Kirgina, M., 2023. Natural Gas Liquids into Motor Gasolines: Methodology for Processing on a Zeolite Catalyst and Development of Blending Recipes. *ChemEngineering*, Volume *7*, p. 93

Bayanov, V.A., Gizetdinova, A.F., Vishnevskaya, A.L., Tagandurdyeva, N.A., Kleymenov, A.V., Trafimov A.V., 2023. Processing Promising Supports for Hydroprocessing Catalysts Based on Flash-Calcined Aluminium Hydroxide. *Oil & Gas Chemistry,* Volume 2, pp. 59–62

Ding, L., Sitepu, H., Al-Bogami, S.A., Yami, D., Tamimi, M., Shaik, K., Sayed, E., 2021. Effect of Zeolite-Y Modification on Crude-Oil Direct Hydrocracking. *ACS Omega*, Volume 6, pp. 28654–28662

Fedushchak, T.A., Uimin, M.A., Maikov, V.V., Mikubaeva, E.V., Akimov, A.S., Morozov, M.A., Zhuravkov, S.P., Petrenko, T.V., Vosmerikov, A.V., Zhirov, N.A., Kogan, V.M., 2019. Two-Component Ni(Co)-Promoted MoS$_2$ Bulk Catalysts and Their Hydrodesulphurising Ability in Model Reactions and Diesel Fraction Hydrotreatment. *Chemistry of Sustainable Development*, Volume 27, pp. 71–77

Fitri, N., Riza, R., Akbari, M.K., Khonitah, N., Fahmi, R.L., Fatimah, I., 2022. Identification of Citronella Oil Fractions as Efficient Bio-Additive for Diesel Engine Fuel. *Designs*, Volume 6, p. 15

Gackowski, M., Podobinski, J., Broclawik, E., Datka, J., 2020. IR and NMR Studies of the Status of Al and Acid Sites in Desilicated Zeolite Y. *Molecules*, Volume 25, pp. 31

Huseynova, G., Muxtarova, G., Aliyeva, N., Gasimova, G., Rashidova, S., 2022. Zeolite-Containing Catalysts in Alkylation Processes. *Catalysis Research*, Volume 2(3, pp. 1–12

Janardhan, H.L., Shanbhag, G.V., Halgeri, A.B., 2014. Shape-Selective Catalysis by Phosphate Modified ZSM-5: Generation of New Acid Sites with Pore Narrowing. *Applied Catalysis A: General*, Volume 471, pp. 12–18

Jaroszewska, K., Lewandowski, M., Góra-Marek, K., Grzechowiak, J., Djéga-Mariadassou, G., 2021. Hydrodesulfurization of 4,6-Dimethyldibenzothiophene and the Diesel Oil Fraction on NiMo Catalysts Supported over Proton-Exchanged AlMCM-41 and TiMCM-41 Extrudates. *Catalysts*, Volume 11, p. 1086

Kar, Y., Göksu, D.S., Yalman, Y., 2018. Characterization of Light Diesel Fraction Obtained from Upgraded Heavy Oil. *Egyptian Journal of Petroleum*, Volume 27, pp. 1301–1304

Laredo, G.C., Pérez-Romo, P., Águeda-Rangel, R., Escobar, J., Vega-Merino, P., 2020. Detailed Characterization of Light Cycle Oil for BTX Production Purposes. *International Journal of Petroleum and Petrochemical Engineering,* Volume 6, Issue 3, pp. 1–12

León, J.N.D., Kumar, C.R., Antúnez-García, J., Fuentes-Moyado, S., 2019. Recent Insights in Transition Metal Sulfide Hydrodesulfurization Catalysts for the Production of Ultra Low Sulfur Diesel: A Short Review. C*atalysts*, Volume *9*, p. 87

Majodina, S., Poswayo, O., Dembaremba, T.O., Tshentu, Z.R., 2023. Towards Improvement of Hydroprocessing Catalysts - Understanding The Role of Advanced Mineral Materials In Hydroprocessing Catalysts. *Minerals and Mineral Materials,* Volume 2, p. 13

Marlinda, Al-Muttaqii, M., Roesyadi, A., Prajitno, D.H., 2022. Formation Of Hydrocarbon Compounds During the Hydrocracking of Non-Edible Vegetable Oils With Cobalt-Nickel Supported On Hierarchical HZSM-5 Catalyst. *In* IOP Conference Series: Earth and Environmental Sciences, Volume 67, p. 012022

Mavai, J., 2022. Methanol Synthesis and Converted into Hydrocarbons Over Zeolite Catalyst a Review. *Journal of Emerging Technologies and Innovative Research*, Volume 9, pp. 221–256

Mustafayeva, R.M., 2012. *Zeolite-Containing Catalysts in The Processes of Obtaining Aromatic Hydrocarbons*. Azerbaijan: Baku

Nikul'shina, M.S., Mozhaev, A.V., Lancelot, C., Blanchard, P., Lamonier, C., Nikul'shin, P.A., 2019. Hydrotreating of Straight-Run Diesel Fraction Over Mixed Nimows/Al_2O_3 Sulfide Catalysts. *Petroleum Chemistry*, Volume 59, pp. 529–534

Prihadiyono, F.I., Lestari, W.W., Putra, R., Aqna, A.N.L., Cahyani, I.S., Kadja, J.T.M., 2022. Heterogeneous Catalyst Based on Nickel Modified into Indonesian Natural Zeolite in Green Diesel Production from Crude Palm Oil. *International Journal of Technology*, Volume 13 (4), pp. 931–943

Rodriguez-Castellon, E., Jimenez-Lopez, A., Eliche-Quesada, D., 2008. Nickel And Cobalt Promoted Tungsten and Molybdenum Sulfide Mesoporous Catalysts For Hydrodesulfurization. *Fuel*, Volume 87, pp. 1195–1206

Saih, Y., Segawa, K., 2009. Catalytic Activity of CoMo Catalysts Supported on Boron-Modified Alumina for the Hydrodesulphurization of Dibenzothiophene and 4,6-Dimethyl Dibenzothiophene. *Applied Catalysis A*, Volume 353, pp. 258–265

Salnikov, V.A., Polyakov, N.A., Nevolina, S.A., Korotkova, N.V., Reznichenko, I.D., Ovchinnikov, K.A., 2023. A Promising Catalyst for Hydrotreating Diesel Fuels on A

Carrier Made of Thermally Activated Aluminum Hydroxide. *Oil & Gas Chemistry,* Volume 2, pp. 49–52

Shakiyeva, T.V., Sassykova, L.R., Khamlenko, A.A., Dzhatkambayeva, U.N., Sassykova, A.R., Batyrbayeva, A.A., Zhaxibayeva, Z.M., Ismailova, A.G., Sendilvelan, S., 2022. Catalytic Cracking of M-100 Fuel Oil: Relationships Between Origin Process Parameters and Conversion Products. *Chimica Techno Acta*, Volume 9(3), p. 20229301

Sikkander, A. M., Kavitha, K., Ramanachiar, R., Anitha, V., Sasikala, S., Sivaraj, C., Balu, T.N., Mishra, S.R., Yasmeen, K., 2022. Hydrodesulphurization of Petroleum. *Petroleum and Chemical Industry International,* Volume 5 (3), pp. 150–152

Suhartono, Romli, A., Hari Prabowo, B., Kusumo, P., Suharto, 2023. Converting Styrofoam Waste into Fuel Using a Sequential Pyrolysis Reactor and Natural Zeolite Catalytic Reformer. *International Journal of Technology*, Volume 14 (1), pp. 185–194

Tanimu, A., Tanimu, G., Ganiyu, S.A., Gambo, Y., Alasiri, H., Alhooshani, K**.**, 2022**.** Metal-Free Catalytic Oxidative Desulfurization of Fuels. A Review. *Energy & Fuels*, Volume 36 (7), pp. 3394–3419

Tuktin, B., Zhandarov, E., Nurgaliyev, N., Tenizbayeva, A., Shapovalov, A., 2019. Hydrotreating of Gasoline and Diesel Oil Fractions Over Modified Alumina/Zeolite Catalysts. *Petroleum Science and Technology*, Volume 37, pp. 1770–1776

Tuktin, B.T., Omarova, A.A., Saidilda, G.T., Sassykova, L.R., 2022. Modified Zeolite Catalysts for Efficient Processing Of N-Hexane and Gasoline Fraction. *Rasayan Journal of Chemistry*, Volume 15, pp. 2442–2449

Tuktin, B.T., Temirova, A.M., Omarova, A.A., Myltykbaeva, Z.K., Anisimov, A.V., 2021. Aromatization of Low-Molecular-Weight Hydrocarbons on Modified Zeolite Catalysts. *Theoretical Foundations of Chemical Engineering*, Volume 55, pp. 1016–1022

Wei, Q., Zhang, P., Liu, X., Huang, W., Fan, X., Yan, Y., Zhang, R., Wang, L., Zhou, Y., 2020. Synthesis of Ni-Modified ZSM-5 Zeolites and Their Catalytic Performance in n-Octane Hydroconversion. *Frontiers in Chemistry*, Volume 8, p. 586445

Wei, Y.J., Zhang, Y.J., Zhu, X.D., Gu, H.M., Zhu, Z.Q., Liu, S.H., Sun, X.Y., Jiang, X.L., 2022. Effects of Diesel Hydrocarbon Components on Cetane Number and Engine Combustion and Emission Characteristics. *Applied Sciences*, Volume 12, p. 3549

Williams, D.B., Carter, C.B., 2009. *Transmission Electron Microscopy*. New York, USA: Springer

Winarto, D.A., Liza, C., Fathurrohman, M.I., Masa, A., Chalid M., 2024. Study of Solvent and Catalyst in Diimide Biphasic Hydrogenation System of Natural Rubber. *International Journal of Technology,* Volume 15 (2), pp. 414–424

Zhang, D., Duan, A., Zhao, Z., Xu, C., 2010. Synthesis, Characterization and Catalytic Performance of NiMo Catalysts Supported on Hierarchically Porous Beta-KIT-6 Material in The Hydrodesulfurization of Dibenzothiophen. *Journal of Catalysis*, Volume 274, pp. 273–286

Zhang, M., Qin, B., Zhang, W., Zheng, J., Ma, J., Du, Y., Li, R., 2020. Hydrocracking of Light Diesel Oil over Catalysts with Industrially Modified Y Zeolites. *Catalysts*, Volume 10, p. 815

Zhang, W., Fang, D., Huang, G., Li, D., Zheng, Y., 2023. Research and Application Development of Catalytic Redox Technology for Zeolite-Based Catalysts. *Catalysts*, Volume 13, p. 1197