

Synergistic Mixed Carbide Catalysts for Accelerated Aerobic Oxidative Desulfurization of Fuels

Argam Akopyan,* Artur Aghoyan, Ekaterina A. Eseva, Maxim O. Lukashov, Mikhail M. Belov, and Davit Davtyan



carbide catalysts (FeMoWC) synthesized rapidly by microwave irradiation for AODS process. The combination of a ternary mixture of carbides for AODS leads to a significant increase in catalytic activity compared to singlephase, dicarbides or simply oxides of transition metals. The synthesized materials were characterized in detail by a complex of methods: XRD, HRTEM, EDX, SEM, XPS, low-temperature nitrogen adsorption/desorption, H₂-temperature-programmed reduction (TPR), Raman spectroscopy. Under



selected conditions (150 °C, 6 atm, 0.5 wt % catalyst dosage) complete oxidation of dibenzothiophene (DBT) was achieved in just 20 min. Under optimal conditions, the specific catalytic activity was 12.73 and 293.43 mmol g^{-1} h⁻¹ for the model and real fuel, respectively. A possible mechanism for the reaction is discussed, including the activation of atmospheric oxygen with the formation of a superoxide radical, the formation of alkyl peroxides and peroxo complexes. The proposed approaches open up wide possibilities for the future development of highly efficient AODS catalysts for practical application and production of clean motor fuels.

1. INTRODUCTION

Despite the rapid growth of clean energy technologies, conventional hydrocarbon fuels still dominate in transportation and energy industries.¹ Therefore, the task of reducing the negative impact of traditional motor fuels and their combustion products on the environment is particularly relevant. Sulfur containing compounds are one of the main pollutants in traditional motor fuels. This is because that the combustion of organosulfur compounds produces sulfur oxides, which are toxic substances for both human health and the environment.² Therefore, in most modern environmental standards, the total sulfur content is one of the key indicators characterizing the environmental friendliness of fuel.³ This explains why desulfurization is one of the most important stages for obtaining high-quality motor fuels.

The main process aimed at reducing the sulfur content in petroleum distillates is hydrotreating. In this process under high hydrogen pressure organosulfur compounds are converted into hydrocarbons and hydrogen sulfide, which is further converted into elemental sulfur.⁴ This is one of the reasons for the problems of elemental sulfur utilization.⁵ The quality of petroleum feedstock has recently declined significantly, which, in particular, leads to an increase in the sulfur content in the feedstock. The deterioration in the quality of petroleum feedstock creates a significant load on hydrotreating processes and stimulates the search for new hydrogen-free sulfur removal methods.⁶

Among the existing hydrogen-free sulfur removal methods, extraction,⁷ adsorption,^{8,9} biodesulfurization,¹⁰ and oxidative desulfurization¹¹ should be highlighted. The most promising method is oxidative desulfurization, which allows obtaining fuels with ultralow sulfur content. The method is based on the oxidation of sulfur-containing components of fuels to polar products—sulfoxides and sulfones. This products can be further extracted by standard extraction or adsorption methods. Various agents are used as oxidizers for the oxidative desulfurization method, including hydrogen peroxide,¹² ozone, alkyl peroxides, sodium hypochlorite, and atmospheric oxygen.¹³ At the same time, interest in aerobic oxidative desulfurization (AODS) has recently increased sharply. This process uses the most accessible and preferred oxidizer atmospheric oxygen.¹⁴

Despite its attractiveness due to the simplicity of implementation, the AODS method faces a number of challenges, in particular those related to the inertness of the oxygen molecule and the need for its activation.^{15–17} Therefore, for the development of the AODS method, it is of fundamental importance to develop highly effective catalysts

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Figure 1. Preparation of catalysts.

capable of activating the oxygen molecule and promoting the selective oxidation of sulfur-containing components in complex hydrocarbon environments. Various catalysts for aerobic oxidative desulfurization are known in the literature, in particular noble metals,¹⁸ polyoxometalates,¹⁹ metal com-plexes,²⁰ metal-free catalysts,⁹ various transition metal oxides.²¹ Catalysts based on noble metals exhibit high activity in the AODS process, but their high cost limits the practical use of such catalysts. Despite a large number of works devoted to the development of catalysts for aerobic oxidative desulfurization, there are still key problems that complicate the practical implementation of this process. Among these problems, it is especially worth noting: relatively low activity of catalysts, which requires a significant increase in reaction time. Thus, if in the presence of hydrogen peroxide, modern catalysts allow achieving 100% conversion of model fuel containing dibenzothiophene²² in just 5 min or less, then aerobic oxidation processes with atmospheric oxygen require hours. Another important problem is the selectivity of oxidation, since AODS requires elevated temperatures above 100 °C, at which oxidation of hydrocarbon components of fuels is possible. Since most of the known AODS catalysts were often tested on model fuels, where the problem of selective oxidation is practically absent, it is not obvious whether they can be used for aerobic oxidative desulfurization of real hydrocarbon fractions. Therefore, the selectivity of oxidation determines both the possibility of oxidation of real fractions and the amount of product loss during purification. In addition, the third key problem in the development of catalysts is the simplicity of its synthesis and the use of industrially available components, which will allow scaling the obtained results in practice.

Previously, we synthesized a catalyst for AODS, which is a mixed iron-tungsten carbide obtained by microwave synthesis in just 15 min from the corresponding oxides and carbon.²³ It was shown that iron oxides on the surface are responsible for the activation of oxygen molecules with the formation of a superoxide radical, while tungsten oxides located on the surface of the hydrophobic carbide are responsible for the formation of active peroxo complexes that oxidize sulfur-containing substrates. The catalysts were tested both on model fuel and on straight-run gasoline fraction. At the same time, the relatively low activity, which negatively affects the oxidation time and catalyst dosage, remains a challenge.

In this work, a mixed synergistic FeMoWC catalyst obtained by microwave irradiation from the corresponding available oxides was developed for the first time. It was shown for the first time that the addition of molybdenum carbide to the composition significantly increases the catalyst activity. The effect of the molybdenum-tungsten ratio on both dibenzothiophene conversion and the peroxide decomposition process was studied. It was shown that the synergistic mixed carbide catalyst FeMoWC operates significantly better than individual FeMoC and FeWC analogues, and a detailed study of the causes of such catalyst behavior is carried out. A systematic study of the effect of oxidation conditions on the desulfurization process was carried out. It was shown that the catalyst allows achieving 100% dibenzothiophene conversion in a wide temperature range from 100 to 150 °C, while an increase in temperature allows for a significant reduction in the oxidation time down to 20 min. The possibility of using a mixed carbide catalyst for deep aerobic oxidative desulfurization of a real sample of diesel fraction with a high initial sulfur content (1.01%) has been demonstrated for the first time. The results obtained in the work can be used in the practical implementation of the aerobic oxidative desulfurization method for obtaining high-quality components of modern motor fuels.

2. EXPERIMENTAL SECTION

2.1. Materials. The following reagents were used to obtain the catalysts: molybdenum oxide (MoO_3 , Sigma-Aldrich, >99.5%, p.a.), tungsten oxide (WO_3 , Sigma-Aldrich, >99.5%, p.a.), iron(II) oxide (FeO, Sigma-Aldrich, >99.5%, p.a.) and carbon (CABOT, Vulcan XC-72R).

The following reagents were used for the oxidation reactions: dibenzothiophene (DBT, Sigma-Aldrich, 98%), 4-methyldibenzothiophene (4-MDBT, Sigma-Aldrich, 96%), 4,6-dimethyldibenzothiophene (4,6-DMDBT, Sigma-Aldrich, 97%), benzothiophene (BT, Sigma-Aldrich, 98%), thioanisole (MeSPh, Sigma-Aldrich, >99%), decalin (Donchim, 99%), straight-run diesel fraction (Moscow Oil Refinery).

2.2. Catalyst Preparation. The synthesis of mixed carbides doped with Fe (FeMoWC) with different proportions of Mo and W carbides was done by taking the stoichiometric ratio of raw materials by general eqs 1, 2 and 3, where the ratios of raw mixtures were taken in such way that in final products we have (w/w %)

10% Fe₃C + 90% (20% Mo₂C + 80% WC) - nominated as F

eMoWC 1/4



Figure 2. XRD patterns of obtained catalysts.

10% Fe₃C + 90% (50% Mo₂C + 50% WC) - nominated as F eMoWC 1/1

10% Fe₃C + 90% (80% Mo₂C + 20% WC) – nominated as F eMoWC 4/1

 $2MoO_3 + 7C = Mo_2C + 6CO$ (1)

 $WO_3 + 4C = WC + 3CO$ (2)

$$3FeO + 4C = Fe_3C + 3CO \tag{3}$$

As precursors were used high purity powders of molybdenum oxide MoO_3 , tungsten oxide WO_3 , iron(II) oxide FeO and carbon C. The powders containing stoichiometric calculated MoO₃, WO₃ and C (w/ w) were weighed and placed in the glass flask and mixed with a magnetic stirrer for 1 h then the mixture additionally was stirred in an agate mortar for 20 min. Part of the mixture was loaded into a quartz flow reactor, purged with nitrogen (99.99%) for 15 min. Details of the flow reactor setup and microwave synthesis can be found in our previous work.²³ After that, the reactor in a vertical position was lowered into a microwave oven. The mixture was subjected to microwave irradiation at 900 W up to incandescence and kept the irradiation for over 10 min until the end of the reaction. The average temperature of the incandescence area of above-mentioned reaction systems was measured to be about 1100–1200 $^\circ C$ by an optical pyrometer (Dostman HT-1800), through a special hole made in the rear wall of the MW oven. Continuously flowing nitrogen (25 mL/

min) was used during the synthesis. The catalyst preparation process is shown in Figure 1.

2.3. Catalytic Experiments. To obtain a model mixture of the substrate with a total sulfur content of 500 ppm, 1.4 mmol (0.258 g) of dibenzothiophene (DBT) were added to 100 mL of decalin. The mixture was stirred and analyzed for component content by GC. Solutions of other sulfur-containing compounds were prepared similarly.

The oxidation reaction was carried out in a 50 mL steel autoclave. The autoclave was loaded with 26 mg of catalyst (0.5 wt %), 6 mL of the model solution of a sulfur-containing substrate in decalin with a sulfur content of 500 ppm, and a stirrer. Next, the air was pumped in to achieve the required pressure. The autoclave was heated in an oil bath to the reaction temperature. The reaction was carried out with constant stirring at 600 rpm for 2 h. Then the autoclave was cooled in cold water to room temperature, opened, and the sample was removed. Reaction products were analyzed by GC-FID with absolute calibration method (Kristal 2000 M) equipped with a capillary column (ZB-1 liquid phase, 30 m \times 0.32 mm). Catalytic experiments were performed at least 3 times each experiment. If the relative difference in conversion between experiments did not exceed 5%, then the average value was taken as the conversion value. A blank experiment without adding catalyst was also carried out 3 times under the following conditions: 120 °C, 1 h, 6 atm, 600 rpm.

The analysis of the model mixture and determination of the substrate content was carried out by gas chromatography (GC) using the absolute calibration method on a "Crystal-2000M" chromatograph with a flame ionization detector, Zebron column (L = 30 m, d = 0.32 mm), ZB-1 liquid phase, with temperature programming from 100 to 250 °C. The concentration was determined by the change in the

relative area of the peaks of the substrate and products (in wt %). The substrate conversion rate was calculated using the following equation

$$\eta = [(C_0 - C_t) / C_0] \times 100\%$$

where C_0 is the initial concentration of the substrate in the model mixture, and C_t is the concentration of the substrate obtained at time *t*.

2.4. Catalytic Desulfurization of Straight-Run Diesel Fraction. The autoclave was loaded with 6 mL of fuel, 0.5 wt % catalyst, and a stirrer. Then the autoclave was hermetically sealed and pumped with air to the pressure of 6 atm. The autoclave was placed in a preheated oil bath at a predetermined temperature. The temperature was varied from 100 to 170 °C. The reaction was carried out with constant stirring at 600 rpm for 2 h. After the completion of the reaction, the autoclave was cooled for 20 min in water bath until the pressure was stabilized. The catalyst was separated from the hydrocarbon phase by centrifugation. The oxidized gasoline fraction was washed with methanol (1:1 by volume). Then the sulfur content in the purified fraction was analyzed.

The sulfur content of the initial diesel fraction and after desulfurization was determined by energy-dispersive X-ray analysis with an ASE-2 sulfur analyzer (Burevestnik Research and Production Enterprise, Russia).

2.5. Characterization. X-ray phase analysis was performed on a Rigaku Rotaflex D/max-RC instrument using copper Cu K_a-radiation ($\lambda = 0.154$ nm). The diffraction pattern from the sample was registered in the angular range $2\theta = 10 - 120^{\circ}$ with a step of 0.02° and a recording rate of 2 deg min⁻¹. Quantitative phase analysis was carried out by the corundum number method using the MDI JADE program.

The Raman spectra were recorded on a Horiba LabRAM HR Evolution spectrometer. To excite the Raman spectra, a HeCd laser with a wavelength of 633 nm was used. Spectral resolution was 3 $\rm cm^{-1}$.

The N₂ adsorption–desorption isotherms at 77 K were investigated using a Gemini VII 2390 (V1.02t) surface area and porosity analyzer (Micromeritics Instrument). Before measurements, the samples were degassed at a temperature of 300 °C for 6 h. The surface area was calculated by the Brunauer–Emmett–Teller (BET) method based on adsorption data in the range of relative pressures $P/P_0 = 0.05-0.2$. The total pore volume was determined based on the amount of adsorbed nitrogen at a relative pressure $P/P_0 = 0.95$. The volume of micropores was determined using the t-plot method.

The sample crystal structure was studied with help of transmission electron microscopy of high-resolution (HR TEM) using transmission electron microscope JEOL JEM-2100 UHR. The sample suspensions were dropped onto Lacey Formvar/carbon films on copper TEM grids (Ted Pella, Inc.). The accelerating voltage was set to 200 kV. Scanning electron microscopy (SEM) of the obtained samples was performed using a Carl Zeiss NVision 40 microscope equipped with an Oxford Instruments X-Max analyzer (80 mm²).

Temperature-programmed reduction with hydrogen (TPR-H₂) was carried out on the Autosorb iQ chemisorption analyzer. The studied sample weighing 200–300 mg was placed in a quartz reactor. The sample was preheated in a helium flow to 400 °C at a rate of 20 °C/ min to remove adsorbed gases and water. Then, the sample cooled to 130 °C was subjected to reduction with 5% H₂ (+N₂) at a flow rate of 25 mL/min and a heating rate of 15 °C/min to 1030 °C with signal registration by a thermal conductivity detector.

XPS spectra of the surface layers were recorded on an OMICRON ESCA+ spectrometer (OMICRON, Germany). The pressure in the chamber of the OMICRON ESCA+ analyzer was maintained below 8 × 10⁻¹⁰ mbar, the radiation source was the Al anode (AlK_a 1486.6 eV).

3. RESULTS AND DISCUSSIONS

3.1. Catalyst Characterization. Based on our previous study of the FeWC mixed carbide catalyst, we aimed to synthesize a synergistic FeMoWC mixed carbide by introduc-

ing a molybdenum carbide (Mo₂C) phase. The objective was to investigate the synergistic effects of Mo₂C on catalyst's activity and selectivity by varying the relative compositions of Mo₂C and WC in the system. The XRD patterns of the FeMoWC catalysts with compositions 1/4 [10% Fe₃C + 90% (20% Mo₂C + 80% WC)], 1/1 (10% Fe₃C + 90% (50% Mo₂C + 50% WC)), and 4/1 [10% Fe₃C + 90% (80% Mo₂C + 20% WC)] are shown in Figure 2. The identified phases include molybdenum carbide, molybdenum oxides, tungsten carbides, tungsten oxides, metallic iron, tungsten, mixed carbide phases (WMoC₂, Fe₃W₃C), and graphite. Individual XRD patterns of the FeMoWC catalysts are provided in the Supporting Information (Figures S1–S3).

All samples exhibit intense diffraction signals corresponding to the β -Mo₂C phase (PDF# 35-0787) at 2θ values of 34.2° , 38.1° , 39.5° , 52.3° , 61.5° , 69.8° , 74.8° , 75.5° , 81.5° , and 84.9° , which are indexed to the (100), (002), (101), (102), (110), (103), (112), (201), (004), and (202) planes, respectively.^{24,25} Prominent signals for hexagonal WC (PDF# 65-4539) are observed at $2\theta = 31.4^{\circ}$, 35.6° , and 48.3° , corresponding to the (001), (100), and (101) lattice planes.^{25,26} Additionally, reflections of the orthorhombic W₂C phase (PDF# 65-8829) are detected near 34.3° , 37.9° , 39.4° , 52.3° , and 61.6° , corresponding to the (100), (002), (101), (102), and (110) planes.²⁶

Metallic tungsten (α -W, PDF# 04-0806) is identified at 2θ values of 40°, 58°, and 73°, corresponding to the (110), (200), and (211) planes.²⁷ Notably, the intensity of these W reflections increases with higher WO₃ content in the raw mixture, particularly in the FeMoWC 1/4 sample. In this sample, faint reflections of monoclinic WO₃ (PDF# 46-1096) appear at $2\theta = 23.1^{\circ}$, 23.4°, and 24.2°, corresponding to the (002), (020), and (200) planes.^{28,29} Weak signals at $2\theta = 25.7^{\circ}$, 36.8°–37.4°, 52.9°, 59.8°, and 70° are assigned to the monoclinic WO₂ phase (PDF# 32-1393), dominant in the FeMoWC 1/4 sample.³⁰

Furthermore, diffraction peaks corresponding to the orthorhombic α -MoO₃ (PDF# 47-1320) and monoclinic MoO₂ (PDF# 65-5787) phases are identified at $2\theta = 12.8^{\circ}$, 34.6°, 39.5°, and 58.1° for MoO₃, indexed to the (020), (060), (002), and (132) planes, and at $2\theta = 26^{\circ}$, 36.9°, and 53.1° for MoO₂, assigned to the (011), (112), and (220) planes.³¹ These oxides are primarily dominant in the FeMoWC 4/1 sample, where the molybdenum oxide content in the raw mixture is higher.

Minor peaks corresponding to the Fe_3W_3C mixed iron– tungsten carbide phase and residual graphite were also observed.^{32,33} The formation of the mixed Fe_3W_3C carbide phase was detected exclusively in the FeMoWC 1/4 sample. Additionally, all samples exhibited mixed WMoC₂ phases (PDF# 65-8770), with the highest intensities observed in the FeMoWC 1/4 sample, where WC coexists with the mixed phase.

The phase intensities observed in the XRD patterns are consistent with theoretical predictions. In the FeMoWC 4/1 sample, the highest relative intensities are associated with molybdenum carbide, along with significant amounts of molybdenum and tungsten oxides in higher oxidation states, and lower relative amounts of tungsten carbide. The presence of molybdenum and tungsten oxides in higher oxidation states, along with carbon from the precursor materials, suggests incomplete reduction. Conversely, the FeMoWC 1/4 sample exhibits the highest content of tungsten carbide and metallic



Figure 3. Raman spectra of the samples.

tungsten, with comparatively lower amounts of tungsten oxides than molybdenum oxides. The distinctive reflection at 2θ = 12.8° in the FeMoWC 4/1 sample corresponds to molybdenum trioxide, which was used as a precursor.

For comparison, the XRD pattern of the FeMoC sample is also presented (Figure S4). It primarily contains three phases: molybdenum carbide, molybdenum dioxide, and metallic molybdenum, without the formation of distinct mixed carbide phases.

The Raman spectroscopy results confirm the X-ray diffraction data (Figure 3). All samples are characterized by the presence of a carbon component with typical distinct bands of disordered graphite (D) and crystalline graphite (G) at 1350 and 1600 cm⁻¹.^{33,34} The G-band characterizes graphene in the plane of the sp² vibrational mode (E_{2g} mode)—this parameter reflects the degree of crystallization of the material. The Dband displays the degree of structural disorder (disorder) near the edge of the microcrystalline structure, which reduces the symmetry of the structure (A_{1g} mode). The presented Raman spectrum also confirms the presence of metallic phases. The bands at 804-810 and 712-714 cm⁻¹ are characteristic of W-C stretching vibrations, the peaks at 266-267 and 325 cm⁻¹ are attributed to O-W-O bond deformation modes, the bands at 184 cm⁻¹ are attributed to lattice vibrations of the hexagonal structure of tungsten trioxide, and 131-136 cm⁻¹ are attributed to the vibrational modes of the $(W_2O_2)_n WO_3$ chain.^{35–37} For the FeMoWC 1/4 sample, bands are observed at 223 and 294 cm⁻¹, which may be attributed to Fe-O or Fe-C bond vibrations.³⁸ The Raman spectra of FeMoWC 1/1 and 1/4 samples are almost identical to each other, while the spectrum of FeMoWC 4/1 contains other vibrational bands. The FeMoWC 4/1 sample is characterized by typical peaks related to molybdenum carbide located at 670, 817, and 994 cm^{-1.39} Similar vibrations at 670, 817, and 994 cm⁻¹ are observed in asymmetric and symmetric stretching of the Mo= O bond and symmetric vibrations of the Mo–O–Mo bond.⁴⁰ The bands at 114, 127, 155, 243, 283, 289, 337, 378 cm⁻¹ can be attributed to bending of the Mo-O-Mo bond, wagging, twisting of the rigid MoO₄ chain, which may correspond to vibrations of the molybdate ion in the iron molybdate structure.³⁸ However, iron molybdate was not detected by Xray diffraction, due to either a low amount or an amorphous state of the phase in the sample.

The low-temperature nitrogen adsorption/desorption isotherms of the samples were type II according to the IUPAC classification (Figure 4).⁴¹ Note that the isotherm for the



Figure 4. Nitrogen adsorption/desorption isotherms for FeMoWC catalysts.

obtained samples was practically undetectable due to the low specific surface area, the value of which didnnt exceed 10 m²/g.⁴² This is explained by the fact that the materials are nonporous, and the main contribution to the specific area come from the outer surface of the particles. It should be noted that with an increase in the content of molybdenum carbide in the samples, an increase in the amount of absorbed nitrogen and, accordingly, the surface area according to BET was observed (Table 1). Note also that a sharp increase in the amount of absorbed nitrogen in the range of $P/P_0 = 0.8-1.0$ indicates a large number of macropores. The voids between the particles form channels and pores for additional adsorption of nitrogen molecules, which was recorded the high average pore

Table 1. Textural Characteristics of FeMoWC Catalyst Samples

FeMoWC	$S_{\rm BET} \left({\rm m}^2/{\rm g} \right)$	$S_{\rm external} ({\rm m}^2/{\rm g})$	$V(\text{cm}^3/\text{g})$	D(nm)
1/4	6	5	0.014	9.11
1/1	8	6	0.041	19.90
4/1	10	9	0.028	10.55
4/1 regen	10	7	0.038	15.10

diameter and low pore volume (the effect of particle agglomeration). As for the regenerated sample of the FeMoWC 4/1 composition, its textural characteristics were preserved after several stages of recycling and regeneration.

The surface morphology of the samples was also studied by SEM (Figure 5). The FeMoWC 4/1 sample mainly consists of



Figure 5. SEM micrographs of FeMoWC 4/1 sample.

nanosized particles with a spherical structure. Agglomerates of various shapes are carbide particles, on the surface of which the formation of spherical particles of transition metal carbides and a residual amount of unreacted carbon are noted.

The morphology of the samples was studied by TEM (Figure 6). The FeMoWC 4/1 sample consists of a carbon substrate resembling agglomerates of arbitrary shape with an average size of 10-20 nm. The carbon part is amorphous graphene layers, the interplanar distance between the layers is 0.34 nm which corresponds to (002) planes of graphite.^{25,43} Nanosized metal particles of various structures are localized on the carbon surface: spherical and needle-shaped. Spherical particles probably belong to the carbide phases of the sample with an average size of 10 - 15 nm, and needle-shaped particles are attributed to the original forms of oxide phases.⁴⁴

High-resolution TEM (HRTEM) images of FeMoWC 4/1 sample show well-defined lattice fringes of the hexagonal Mo₂C phase with an interplanar spacing of 0.26 nm, that can be assigned to the (010) planes of Mo₂C,⁴⁵ WC phase which interplanar distance is 0.25 nm corresponding to (100) planes of hexagonal WC,⁴⁶ where both carbide phases encapsulated with a regular graphitic shell which is also visible in TEM micrographs. Latter have been observed for other microwave produced nanoparticles when a carbon-based susceptor has been used.^{47,48}

Uniform distribution of metal particles is noted. According to EDX mapping analysis, metal particles (Fe, Mo and W) are uniformly distributed throughout the volume of the carbon substrate.

The oxidation-reduction activity of the surface was studied by the method of temperature-programmed reduction with hydrogen (TPR-H₂). The TPR-H₂ curve of the FeMoWC 1/4 sample shows four main signals: one intense signal at 800 °C, the second signal appearing at 700 °C, and the third signal at 490 °C (Figure 7). It is assumed, based on the XRD data and literature presented in Table 2, that the peak at 490 °C may be a partial reduction of Fe³⁺-Fe²⁺, 630 °C, according to literature data, corresponds to the reduction of Fe²⁺-Fe⁰, 700 °C corresponds to the complete reduction of molybdenum Mo⁴⁺-Mo⁰ contained in the catalyst. The signal at 800 °C corresponds to the complete reduction of tungsten $W^{4+}-W^0$ which agrees with the XRD data, where tungsten oxide phases are recorded. On the TPR-H₂ curve of the FeMoWC 1/1 sample, peaks are observed at 430, 630, 700, and 800 °C, corresponding to the transitions Mo⁶⁺-Mo⁴⁺, Fe²⁺-Fe⁰, Mo⁴⁺-Mo⁰ and W⁴⁺-W⁰. The inflection observed at 340 °C presumably corresponds to the partial reduction of tungsten $W^{6+}-W^{4+}$. It should be noted that the transition $Mo^{6+}-Mo^{4+}$ is shifted due to the different environment of molybdenum atoms and, as a consequence, the effect on the partial reduction temperature. For the FeMoWC 4/1 sample, the main signals are observed: 430, 600 and 700 °C, as well as an inflection at 340 °C, which corresponds to the transitions $Mo^{6+}-Mo^{4+}$, $Fe^{2+}-Fe^{0}$, $Mo^{4+}-Mo^{0}$ and $W^{6+}-W^{4+}$.

Thus, transition metal oxides in various oxidation states were found on the surface of the obtained carbide materials. It should be noted that the reduction curves of the FeMoWC 1/4 and FeMoWC 1/1 samples are identical to each other, and the FeMoWC 4/1 sample has a different unique composition characterized by its own set of oxidation-reduction transitions. The most indicative are high-temperature transitions, in particular, for the obtained samples, the highest signal intensity in the high-temperature region corresponds to the reduction of molybdenum and tungsten in the intermediate oxidation state of 4+. Namely, for the FeMoWC 1/4 and FeMoWC 1/1 samples, the high-temperature transition W4+-W0 is noted, and for the FeMoWC 4/1 sample this transition is absent, which correlates with the results of Raman spectroscopy. The peculiarity of the redox behavior of the samples is directly related to their composition and will probably affect the catalytic activity in the oxidation reaction of sulfur-containing compounds.

To determine the valence state and chemical composition, XPS analysis of the samples was performed. According to the survey spectrum, each sample contains chemical elements Mo, W, O, C and low-intensity lines of Fe, the profiles of which were separately analyzed to confirm the presence of bonds (Figures S5–S7).

In the Fe $2p_{3/2}$ spectra, peaks of Fe³⁺ and Fe²⁺ with their corresponding satellites were found (Figure 8). Peaks at binding energies (BE) of 710.4 and 713 eV correspond to the Fe²⁺ and Fe³⁺ states with corresponding satellites at BE of 715.4 and 719.6 eV^{52} . For the extreme samples 1/4 and 4/1, peaks were found at 707.4 eV corresponding to the Fe-C bond.⁵³ It should be noted that due to the low intensity of the Fe 2p spectrum and the complexity of the state shape curves, it is not possible to unambiguously isolate the states.⁵⁴ The Mo 3d profile is described by a complex, multicomponent composition of various molybdenum states. The threedimensional spectrum contains Mo^{6+} , Mo^{4+} , $Mo^{\delta+}$, Mo^{3+} , Mo⁰. The extremum at the binding energy of 232.8 eV corresponds to molybdenum in the highest oxidation state, which may indicate the presence of molybdenum trioxide as the initial component in the composition of the samples. The low-intensity peak at 231.9 eV also corresponds to Mo⁶⁺ in the structure of the molybdate ion, which indicates the possible formation of compounds based on iron molybdate, which is in good agreement with the results of Raman spectroscopy. Two peaks at the BE of 230.6 and 229.8 can be attributed to the species Mo⁴⁺ and Mo³⁺. Peaks at the BE of 229.8 eV is attributed to $Mo^{\delta+}$ (2 < δ < 4), that may indicate the formation



Figure 6. TEM images of FeMoWC 4/1 (inset: the particle size distribution); HRTEM images of FeMoWC 4/1. Corresponding elemental mapping of Fe, Mo, W.



Figure 7. Temperature-programmed recovery curves of FeMoWC samples.

of a Mo oxycarbide phase.⁵⁵ The diversity of the valence states of molybdenum indicates a gradual reduction of the initial MoO_3 in the presence of carbon under microwave radiation. The Mo^0 was also detected at the binding energy of 228.5 eV, indicating the formation of a carbide component and metallic

Table 2. Proposed Interpretation of TPR-H₂ Signals Based on Literature Data

temp. (°C)	possible transitions of oxidation state	ref
340	$W^{6+} - W^{4+}$	49
430	Mo ⁶⁺ -Mo ⁴⁺	50
490	$Mo^{6+}-Mo^{4+}$, $Fe^{3+}-Fe^{2+}$	50,51
600	$Fe^{2+}-Fe^{0}$	51
630	$Fe^{2+}-Fe^{0}$	51
700	Mo ⁴⁺ -Mo ⁰	50
800	$W^{4+}-W^{0}$	49

molybdenum in the obtained materials.^{38,52,56,57} The W 4f profile also has a variety of valence states of tungsten, where the formation of both carbide and oxide phases is observed. Peaks at 36.1 and 35.5 eV are noted, which are attributed to W^{6+} in WO₃ and WO₄²⁻ and a peak at and 32.4 eV, related to W^{4+} , respectively. The formation of tungsten carbide confirms



Figure 8. XPS spectra of levels Fe 2p, Mo 3d, W 4f, O 1s, C 1s of FeMoWC samples.

the presence of the W^0 at a binding energy of 31.9 eV.⁵⁸⁻⁶⁰ The O 1s spectrum contains four deconvoluted peaks at binding energies of 533.3, 532.3, 531.5, and 530.9 eV, which can be attributed to adsorbed water or oxygen (H_2O) , carbon dioxide (C=O), adsorbed surface hydroxyl groups (C-O, OH), and lattice oxygen (O_{lat}) of metal oxides.^{59,61} It is known that adsorbed oxygen-containing particles on the surface of catalysts, in particular H2O, CO, OH, contribute to the improvement of adsorption and activation of oxygen molecules.^{62,63} This indicator (O_{ads}) plays an important role in promoting the aerobic oxidation reaction and has a direct relationship with catalytic activity. According to the Table S1, the FeMoWC 4/1 catalyst demonstrates the highest O_{ads}/O_{lat} ratio, which indicates a large number of oxygen vacancies in the sample, unlike other catalysts. The C 1s level spectrum consists of four deconvoluted peaks localized at binding energies of 289.6, 288.4, 286.6, 284.5, and 283.8 eV corresponding to typical O=(C)-OH, O=(C)-O, C-O, C-C, M-C (carbide phase).^{59,64,65} The formation and presence of carbide and oxide phases in the samples are well confirmed by the C 1s and O 1s level spectra, which is consistent with both the XRD and Raman spectra.

According to the obtained XPS data, a large valence diversity of the elements included in the samples is observed, as well as the presence of both carbide and oxide components. Moreover, the carbide phase is present in the composition of iron, tungsten, and molybdenum, and the oxide phase exists only in the composition of tungsten and molybdenum. This is probably due to the difference in the reduction rate of the oxides used as initial reagents, which is due to the kinetic factors of the formation of the corresponding carbide phases. In the HSC 10 program it is calculated that the formation of molybdenum carbide is mostly favorable than tungsten carbide as molybdenum carbide formation reaction constant is like 10^{21} but the reaction constants of formation of WC and W₂C are 10^{13} and 10^{7} . In addition, this indicates that the target reaction of metal oxide reduction with the production of polyphase samples of different compositions is incomplete. In all spectra for all elements, a decrease in the elements in the highest and intermediate oxidation state toward an increase in the carbide phase is observed. Detailed information on the XPS data, including the peak name, its correlation depending on the position (binding energy), the percentage content by area for different multiplicities and the total content, is supplemented in Tables S2-S4.

In conclusion, it should be noted that the XPS results of the surface of the obtained samples to some extent contradict the XRD results. According to the XRD patterns, the main share of the sample is occupied by molybdenum and tungsten carbides formed during the reduction. While according to the XPS studies, the relative content of the oxide component prevails over the content of carbide phases. Apparently, this is due to the gradual oxidation of transition metal carbides with the formation of oxo-carbides and/or oxides in the intermediate and highest oxidation state. The smooth transition of the signal intensities corresponding to the metal-carbon bond toward an increase in both the oxidation state and the intensities of the corresponding signals confirms the oxidation of the surface and the formation of oxides on the surface. The presence of metal compounds in intermediate oxidation states can promote the process of aerobic oxidation, according to data known in the literature.⁶⁶ Moreover, such a feature is observed for all three metals contained in the obtained samples. The above agrees

well with the results of Raman spectroscopy and temperatureprogrammed reduction with hydrogen.

Thus, the following conclusions can be made based on the physicochemical characteristics of the studied samples:

- According to X-ray diffraction, the obtained samples mainly consist of carbide phases of the corresponding transition metals. Low-intensity reflexes of oxide forms of metals are noted, both in the highest and intermediate oxidation states. Mixed carbide phases of iron-molybdenum, molybdenum-tungsten were found in the obtained samples. The largest number of oxide phases is observed in the FeMoWC 4/1 sample.
- Characteristic vibrations of metal—carbon and metal oxygen bonds were found in the Raman spectra. The spectrum of FeMoWC 4/1 differs significantly from other samples. This is probably due to the composition of the sample and the high content of molybdenum carbide, the surface of which is easily oxidized in air with the formation of oxo-carbides and/or oxides in an intermediate oxidation state.
- The obtained samples are nanosized nonporous materials with a poorly developed surface area, the value of which does not exceed 10 m²/g.
- According to SEM and HRTEM, the carbide and oxide components of the samples are uniformly distributed on the surface of the carbon substrate and are in a highly dispersed state. The average particle size is 10–20 nm.
- The study of the oxidation-reduction activity of FeMoWC samples showed the existence of transition metal oxides in various oxidation states on the surface. High-temperature transitions for samples with a molybdenum: tungsten ratio of 1/4 and 1/1 correspond to the reduction of W⁴⁺-W⁰, and for the 4/1 sample indicates the reduction of Mo⁴⁺-Mo⁰. The difference in the curves in the high-temperature region is due to the difference in the composition of the samples.
- XPS study of the surface of the samples demonstrates a wide variety of valence states of the elements contained in the samples. The obtained data indicate the formation of oxo-carbides and/or oxides due to oxidation of air on the surface of carbides.

3.2. Oxidation of Model Sulfides. The catalyst activity was compared using a model mixture containing a solution of dibenzothiophene in decalin. This is one of the most common model fuels used in aerobic oxidative desulfurization, which makes it possible to compare the efficiency of the obtained catalysts with their analogues known in the literature. The choice of dibenzothiophene is due to its wide application as a model substrate, as well as its prevalence in petroleum fractions. The choice of decalin is due, on the one hand, to its frequent use in the literature, and on the other hand, to the possibility of forming active alkyl peroxides under the influence of atmospheric oxygen, which can then participate in the oxidation process. We have previously demonstrated the possibility of using mixed carbide FeWC, in which iron ions act as oxygen activators that generate the formation of superoxide radicals.²³ And tungsten oxide located on the carbide surface forms a peroxo complex under the action of alkyl peroxides and oxidizes sulfur-containing substrates. It was shown that the use of carbide allows one to obtain better results compared to pure tungsten oxide, apparently due to the hydrophobic nature of the carbide and its nanoscale structure.

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At the same time, it is known that, as a rule, molybdenum oxides also form peroxo complexes and molybdenum compounds are often more widely used in the process of oxidative desulfurization as catalysts.⁶⁷ In the present work, an approach was used to increase the efficiency of the mixed carbide, in which molybdenum carbide was added to the catalyst. That is, a series was obtained in which both the mixed carbide FeMoC and mixtures with tungsten FeMoWC were used. In this case, iron ions located on the surface provide oxygen activation, and molybdenum and tungsten oxides form active peroxo complexes responsible for the oxidation of sulfurcontaining compounds.

The results of the comparison of the catalyst activity are shown in Figure 9. It should be noted that in the blank



Figure 9. Comparison of catalyst activity. Oxidation conditions: 120 $^{\circ}$ C, 1 h, 0.5 wt % cat., 6 atm, 600 rpm.

experiment, the substrate conversion for 1 h is only 5%. At the same time, molybdenum and tungsten carbides show a result of 0% DBT conversion, which is lower than the blank, and this indicates their oxidation under these conditions and oxygen absorption. Iron carbide shows results comparable to the blank experiment.

When comparing pure molybdenum and tungsten oxides, molybdenum exhibits higher activity, apparently due to the more active formation of peroxo complexes. Tungsten carbide activated by oxidation exhibits higher activity than the original tungsten oxide, which may be due to the smaller particle size and hydrophobicity of tungsten carbide, which allows for more efficient dispersion of the catalyst in a hydrocarbon medium. We have previously shown that by doping tungsten carbide with iron, it is possible to avoid the activation stage, while maintaining the activity of the catalyst.²³ When moving from the mixed carbide FeWC to FeMoC, the conversion of DBT increases sharply from 22 to 43%. That is, the dynamics and difference in activity observed in the case of pure oxides are also preserved when moving to carbide catalysts in which the active phase is the corresponding oxides located on the surface. It is important to note that the highest activity is exhibited by ternary FeMoWC systems containing both molybdenum and tungsten. The results obtained indicate a synergistic effect from the combination of molybdenum and tungsten compounds in the catalyst. In this case, when switching from the FeMoWC 1/ 4 catalyst to FeMoWC 4/1, i.e. with an increase in the molybdenum content, a noticeable increase in DBT conversion from 60 to 77% is recorded. It is interesting that the limiting option-i.e. the catalyst without tungsten FeMoC shows a significantly worse result in DBT conversion equal to 43%. Thus, the obtained results indicate that despite the higher activity of mixed molybdenum carbides and molybdenum oxide compared to tungsten-containing analogues, the use of ternary iron-molybdenum-tungsten systems allows achieving significantly better results. That is, the synergistic effect of the combination of molybdenum and tungsten is clearly manifested.

The study of the dependence of DBT conversion on the mixing rate of the mixture is necessary in order to carry out the process in the kinetic region, in which diffusion limitations are minimized or absent. With an increase in the rotation frequency of the magnetic stirrer from 150 to 600 rpm, the DBT conversion increases due to better dispersion of the catalyst in the reaction medium (Figure 10A). It is important to note that with a further increase in the rotation frequency to 900 and 1200 rpm, the substrate conversion remains virtually unchanged, indicating that the reaction occurs in the kinetic region, since the materials are virtually nonporous and the



Figure 10. Influence of reaction conditions on DBT conversion: effect of stirrer stirring frequency, 120 °C, 1 h, 0.5 wt % cat., 6 atm (A); catalyst dosage, 120 °C, 1 h, 6 atm, 600 rpm (B). Studying the mechanism of the process: the content of alkyl peroxides, 120 °C, 1 h, 6 atm, 600 rpm (C); decomposition of H_2O_2 in the presence of catalysts, 50 °C, 1 h, 2 wt % cat., 600 rpm (D).



Figure 11. Influence of reaction conditions on DBT conversion: temperature, 0.5 wt % catalyst, 6 atm, 600 rpm (A); air pressure, 120 °C, 1 h, 0.5 wt % cat., 600 rpm (B). Studying the mechanism of the process: radical traps, 120 °C, 1 h, 0.5 wt % FeMoWC 4/1, 6 atm, 600 rpm (C). Oxidation of sulfur-containing substrates, 120 °C, 0.5 wt % FeMoWC 4/1, 6 atm, 600 rpm (D). Catalyst recycling, 120 °C, 0.5 wt % FeMoWC 4/1, 6 atm, 600 rpm (E).

reaction presumably occurs on the surface of the catalyst particles. Therefore, a rotation frequency of 600 rpm was used for further experiments.

When varying the catalyst dosage, the DBT conversion changes significantly depending on both the amount of catalyst and the type, i.e. the molybdenum/tungsten ratio (Figure 10B). Thus, in the case of the FeMoWC 4/1 catalyst with the highest molybdenum content, the DBT dependence curve on the dosage has a convex shape and passes through a maximum at a dosage of 1% by weight. At low dosages (0.03-0.13%) by weight), the DBT conversions in the presence of FeMoWC 4/ 1 significantly exceed the values obtained in the presence of other FeMoWC catalysts with a lower molybdenum content. This may be due to the higher activity of molybdenum peroxo complexes in the oxidation of the sulfur-containing substrate compared to tungsten peroxo complexes. It is interesting to note that at high dosages above 2%, a sharp decrease in substrate conversion is observed down to 0% at a dosage of 2.5%. This may be due to the fact that the high molybdenum content prevents the accumulation of alkyl peroxides formed during the reaction under the action of atmospheric oxygen on decalin. It is interesting to note that for the other two catalysts FeMoWC 1/1 and FeMoWC 1/4 the curve of the dependence of DBT conversion on the dosage has a significantly different shape. At the initial stage, with an increase in the dosage from 0.03 to 0.5 wt %, an increase in DBT conversion is observed due to an increase in the number of active sites and an increase in the reaction rate. With a further increase in the dosage from 0.5% to 2 wt % in the case of FeMoWC 1/1, a slow increase in conversion is observed, which is apparently associated with the achievement of equilibrium, at which a further increase in the catalyst dosage, on the one hand, leads to an increase in the number of active sites, and on the other hand, prevents the accumulation of intermediate compounds-alkyl peroxides, which in turn slows down the oxidation process. It should be noted that in the case of FeMoWC 1/4, with increasing dosage, a sharper increase in DBT conversion is observed, i.e. an increase in the tungsten content in the catalyst promotes

the accumulation of alkyl peroxides so that an increase in the catalyst dosage leads to an increase in substrate conversion. Thus, the results of varying the catalyst dosage show that the higher the molybdenum content in the system, the higher the catalyst activity at lower dosages and the more sensitive the DBT conversion is to the excess of catalyst in the system. That is, the presence of tungsten promotes the accumulation of alkyl peroxides and higher catalyst activity at high dosages. The obtained results can also explain why in the presence of the limiting variant—a catalyst without tungsten FeMoC, the DBT conversion is only 43%. Thus, the use of a mixed catalyst combining molybdenum and tungsten allows for a synergistic effect, which achieves a significantly higher substrate conversion than when using each metal separately.

In order to confirm the assumptions about the formation and accumulation of alkyl peroxides, in addition to recording the DBT content, we analyzed the content of decalin alcohol at different catalyst dosages (Figure 10C). As we have shown previously,⁶⁸ during aerobic oxidation of a model DBT mixture in decalin, the presence of decalin alcohol, which is a decomposition product of the corresponding alkyl peroxide, is recorded after the reaction. Therefore, the analysis of the amount of decalin alcohol formed allows us to indirectly estimate the amount of alkyl peroxide formed during the reaction. It should be noted that the profiles of the graphs of the dependence of decalin alcohol concentration on the catalyst dosage correlate well with the DBT conversion curves at different catalyst dosages under the same conditions. Thus, in the presence of the FeMoWC 4/1 catalyst, the graph of the dependence of decalin alcohol concentration on the catalyst dosage also passes through a maximum at the 1% point and decreases to almost zero at a dosage of 2%. And at low dosages, the alcohol concentration is higher compared to catalysts containing a smaller amount of molybdenum. In general, the results obtained confirm the previously made conclusions that high molybdenum concentrations prevent the accumulation of alkyl peroxides. At the same time, the higher the DBT conversion, the higher the content of decalin alcohol in the

final reaction mixture. That is, the more intensely alkyl peroxides are formed and the less they decompose in the presence of the selected catalyst, the higher the DBT conversion.

In order to study the peroxide decomposition issue in the presence of synthesized catalysts in more detail, the decomposition kinetics of a model hydrogen peroxide solution in the presence of mixed FeMoWC carbides was studied. For this purpose, a carbide sample was added to a hydrogen peroxide solution with a peroxide mass fraction of 33% and stirred at a temperature of 50 °C (at higher temperatures, hydrogen peroxide itself begins to decompose intensively even without adding a catalyst). The hydrogen peroxide concentration was monitored by refractometric analysis. The results are shown in Figure 10D. It should be noted that under the selected conditions, in a blank experiment without adding a catalyst, the hydrogen peroxide concentration decreased insignificantly from 33% to 29% in 2 h. The results of studying the dependence of hydrogen peroxide concentration on time in the presence of catalysts with different molybdenum and tungsten ratios show that the higher the molybdenum content in the system, the faster the hydrogen peroxide concentration decreases over time, i.e., the more intensive its decomposition. The obtained data correlate well with the results of aerobic oxidative desulfurization of DBT and the content of decalin alcohol in the reaction. Thus, the data on the decomposition of hydrogen peroxide indicate that with a high content of molybdenum in the catalyst, more intense decomposition of the peroxide is observed. This allows us to assume that in the process of aerobic oxidative desulfurization, the catalyst with a high content of molybdenum FeMoWC 4/1 at high dosages decomposes the resulting intermediate product-decalin hydroperoxide, which prevents its accumulation in the system and, as a result, a low conversion of dibenzothiophene is recorded.

With increasing reaction temperature, an increase in substrate conversion is observed (Figure 11A), which may be associated with an increase in the rate of formation of alkyl peroxides from decalin and correlates well with literature data.⁶⁹ It is important to note that at each of the temperatures, complete oxidation of DBT can be achieved. Moreover, even at a relatively low temperature of 100 °C, at which the aerobic oxidation process is rarely carried out, 100% conversion of dibenzothiophene is achieved in 4 h. For comparison, in the previous work, where mixed carbide without molybdenum FeWC²³ was used, at a temperature of 100 °C and a reaction time of 4 h, the conversion of DBT was about 20%. This also indicates the high activity of the carbide catalyst containing molybdenum in its composition. Increasing the temperature can significantly reduce the oxidation time. Thus, at a temperature of 130 °C, it is possible to achieve complete oxidation of dibenzothiophene in 40 min of oxidation, and at 150 °C—in just 20 min. Such a short oxidation time opens up opportunities for carrying out aerobic oxidative desulfurization in industrial flow systems for cleaning fuel components, where a short reaction time is one of the key requirements for the catalyst and the process. It should be noted that the catalyst has high activity even at low dosages: with a catalyst mass loading of 0.12% and an oxidation temperature of 130 °C, it is also possible to achieve 100% conversion of dibenzothiophene in 1 h of oxidation. For comparison, a previously studied molybdenum-free catalyst (FeWC) made it possible to achieve the same results under the same conditions, but at a dosage of 2%.²³ Further experiments were carried out at a temperature of 120 °C, when, on the one hand, it is possible to achieve almost complete conversion of the substrate in 1.5 h, and on the other hand, it is possible to more clearly see the influence of the variable parameter on the conversion of the studied substrate. To gain a more complete understanding of the DBT conversion process using the FeMoWC 4/1 catalyst, kinetic experiments were conducted (Figure S8). The reaction rate constants k at 100, 110, 120 and 130 °C were 0.0485, 0.0668, 0.1046, and 0.1668 min⁻¹, respectively. The activation energy (E_a) of 51.8 kJ/mol is calculated based on the Arrhenius equation.

The results of oxidation of the model DBT mixture at different air pressures are shown in Figure 11B. According to the obtained data, a monotonic increase in DBT conversion is observed with increasing pressure, which is apparently due to an increase in the solubility of oxygen in the model mixture with increasing pressure. It should be noted that the sharpest increase is achieved in the pressure range from 2 to 6 atm, and a further increase in pressure from 6 to 8 and to 10 atm leads to a less sharp increase in substrate conversion, which may be due to saturation of the system with atmospheric oxygen. Table S5 (Supporting Information) shows the molar oxygen/ sulfur ratios for different pressures. It is evident that even at a minimum pressure of 2 atm, the oxidizer is in large excess compared to stoichiometry (2:1). This also indicates that the increase in substrate conversion with increasing pressure may be due to an increase in the solubility of oxygen in the reaction medium.

In order to investigate the possible pathways of the oxidation reaction, the AODS process was carried out in the presence of radical traps (Figure 11C). According to the results obtained, the addition of radical traps, depending on their nature, significantly affects the conversion of dibenzothiophene. That is, the oxidation reaction proceeds through the formation of free radicals. According to the results obtained, the conversion of DBT is most strongly reduced in the case of adding benzoquinone, which is a known trap for the superoxide radical⁷⁰ That is, as we have previously shown, in the presence of iron ions, oxygen forms a superoxide radical, which, when interacting with decalin, forms the corresponding alkyl peroxide. Under the action of alkyl peroxide on molybdenum and tungsten oxides located on the catalyst surface, the corresponding peroxo complexes are formed, which are effective oxidizers of sulfur-containing compounds.²³ It should be noted that the addition of potassium iodide to the system also leads to a decrease in DBT conversion, but to a lesser extent than with the addition of benzoquinone. Potassium iodide is a known trap for hydroxyl radicals⁷¹ which also indicates the participation of hydroxyl radicals in the oxidation of sulfur-containing compounds, which, apparently, can be formed in the system during the destruction of the resulting alkyl peroxides. The addition of sodium azide leads to a slight decrease in DBT conversion, which indicates an insignificant role of singlet oxygen in the AODS process.

Real samples of petroleum distillates contain a large number of various sulfur-containing compounds, including mercaptans, sulfides, and heteroaromatic sulfur-containing compounds. The latter are the most difficult to remove components in the process of obtaining modern motor fuels that meet strict environmental standards. Oxidation of various types of sulfurcontaining substrates was carried out in the presence of the most active catalyst FeMoWC 4/1 at a dosage of 0.5% by weight (Figure 11D). It should be noted that dibenzothiophene derivatives and methyl phenyl sulfide can be completely oxidized after 1.5 h of oxidation. At the same time, methylsubstituted dibenzothiophenes (MDBT and DMDBT) are slightly worse oxidized compared to DBT in 1 h due to steric hindrances associated with the presence of a methyl group. Benzothiophene is slightly worse oxidized due to the lower electron density on the sulfur atom, the conversion of which is 49 and 83% in 1 and 1.5 h of oxidation, respectively. In general, the obtained results on the reactivity of various types of sulfurcontaining substrates correlate well with the literature data.⁷²

One of the most important characteristics of the catalyst is the possibility of its reuse, including after regeneration. In this work, we investigated the possibility of reusing the FeMoWC 4/1 catalyst in the oxidation of a model mixture under selected standard conditions, under which 100% substrate conversion is not achieved: 120 °C, 0.5% catalyst dosage, 1 h oxidation (Figure 11E). This approach allows us to better determine the changes in substrate conversion with each new oxidation cycle. After oxidation, the catalyst was separated from the reaction mixture by centrifugation and added to a new portion of the model fuel without further processing. It should be noted that a slight increase in DBT conversion from 77 to 80% is observed in the second oxidation cycle, which may be due to the presence of decalin oxidation products on the catalyst surface-decalin alcohol, which promotes the formation of alkyl peroxides involved in the process of aerobic oxidative desulfurization. Overall, substrate conversion is maintained for 5 oxidation cycles without the need for regeneration, which opens up opportunities for further scaling of aerobic oxidative desulfurization in flow-through pilot plants where long catalyst life between regenerations is important.

Based on the results of previous studies⁶⁸ and the physicochemical results of catalyst analyses, the following mechanism can be suggested (Figure 12). At the first stage, atmospheric oxygen is activated by the action of iron ion compounds (located on the catalyst surface) to form a superoxide radical. When the superoxide radical interacts with decalin or decalin alcohol, the corresponding alkyl peroxide is



Figure 12. Proposed mechanism of aerobic oxidation of organosulfur compounds in the presence of FeMoWC catalysts.

formed, which can then interact with molybdenum and tungsten oxides to form active peroxo complexes. Molybdenum and tungsten peroxo complexes are strong oxidizers and oxidize sulfur compounds. It should be noted that with an increase in the molybdenum: tungsten ratio in catalysts composition, according to the XPS results, the content of lattice oxygen and adsorbed oxygen particles increases (Table S1). These particles can participate in oxygen activation, which can explain the higher activity of the catalyst with a higher molybdenum content.

Real hydrocarbon fractions have a complex chemical composition and contain a large number of various sulfurcontaining substrates. Therefore, the results of oxidative desulfurization of model and real mixtures often differ greatly, and in real fuels the process usually proceeds much worse than in model fuels. This is apparently due to the presence of both sterically substituted sulfur-containing substrates and hydrocarbon components (naphthenes, aromatic compounds) capable of being oxidized under the process conditions. Therefore, for a full study of the catalyst efficiency in the process of aerobic oxidative desulfurization, it is necessary to carry out the process of desulfurization of real hydrocarbon fractions. In this work, a straight-run diesel fraction with a high initial sulfur content of 10100 ppm was used as a real fraction. The oxidation process was similar to the oxidation of the model fuel with the only difference that after the reaction, the oxidation products (sulfones) were extracted by a single extraction with an equivalent amount of methanol. Oxidation was carried out in the presence of FeMoWC 4/1 catalyst, which had previously demonstrated the highest activity in the oxidation of model fuel containing dibenzothiophene. Figure 13 shows the dependence of the residual sulfur content on the



Figure 13. Aerobic oxidative desulfurization of straight-run diesel fraction. Oxidation conditions: 2 h, 0.5 wt % FeMoWC 4/1, 6 atm, 600 rpm. Extraction of oxidation products with methanol.

oxidation temperature. According to the obtained results, noticeable oxidation of sulfur-containing compounds is observed already at 100 °C and the total sulfur content decreases to 6524 ppm, which correlates with the results of oxidation of the model fuel, where slow oxidation of DBT was also observed at 100 °C. With an increase in temperature, the residual sulfur content initially decreases, reaching a minimum value of 2610 ppm at a temperature of 150 °C. These results are also comparable with the oxidation data of the model mixture, according to which an increase in the reaction temperature leads to an increase in the substrate conversion. At the same time, it should be noted that with a further increase in the oxidation temperature of the diesel fraction to 170 °C, a

Table 3. Comparison of the Specific Catalytic Activity of Various Catalytic Systems

catalyst	fuel	S- content (ppm)	reaction conditions		conversion/AODS efficiency (%)	specific catalytic activity (mmol g ⁻¹ h ⁻¹)	ref.	
			temp. (°C)	time (h)	catalyst dosage (g/L)			
MoO _x	model fuel (DBT/decaline)	500	120	3	0.25	61	11.33	73
$MoO_x + g-BN$					5	62	0.58	
MoO _x NPs/g-BN					5	100	0.93	
$MoO_3/g-C_3N_4$	model fuel (DBT/dodecane)	200	130	1.66	0.5	100	5.65	74
MoO ₃ /Beta	model fuel (DBT/decaline)	500	90	6	1	100	2.33	75
3DOM WO _x -400	model fuel (4,6- DMDBT/-dodecane)	200	120	4	0.5	99	2.48	76
3DOM W _x TiO ₂	model fuel (DBT/ <i>n</i> -dodecane)	200	120	6	0.5	98	1.63	77
WO ₃ /MMS-500	model fuel (DBT/decaline)	500	120	8	0.5	100	3.50	78
CoMoO ₄ -Co ₃ O ₄	model fuel (DBT/decaline)	500	110	1	0.5	100	28.00	79
Co ₂ MoO	model fuel (DBT/decaline)	500	100	6	5.56	83	0.35	80
CoMo-FMs	model fuel (DBT/decaline)	500	110	2	1	100	7.00	81
MnMoO	model fuel (DBT/decaline)	500	120	1	0.75	100	18.67	63
Fe/ACMB	model fuel (DBT/ <i>n</i> -Decane)	412	25	2	36	13	0.02	82
Fe _n MoO _x	model fuel (DBT/decaline)	500	100	6	0.33	100	7.07	83
CoFeMoO _x	model fuel (DBT/decaline)	500	100	3	1	99	4.62	62
MoO _x /MC-600 MoO _x /MS-600	model fuel (DBT/decaline)	200	120	5	0.5	97	2.33	66
$MoCoFeVN_x$	model fuel (DBT/ <i>n</i> -dodecane)	200	120	8	1	70	0.53	84
Mo ₂ C/C	model fuel (DBT/ hexadecane/ ethylbenzene)	400	70	4	10	25	0.08	85
WC/C	model fuel (DBT/decaline)	500	120	3	4.43	100	1.05	86
Ti_3C_2/Ti_3AlC_2	model fuel (DBT/ <i>n</i> -Dodecane)	200	130	3	1	95	1.58	87
Fe ₃ C	model fuel (DBT/decaline)	500	120	3	4.43	42	0.44	23
FeWC	model fuel (DBT/decaline)	500	120	3	4.43	100	1.05	23
			130	2	4.43	100	1.58	
			130	1	17.73	100	0.79	
	straight-run gasoline	1000	150	2	13.3	99	1.04	
FeMoWC4/1	model fuel (DBT/decaline)	500	130	1	1.1	100	12.73	this work
			150	20 min	4.43	100	9.48	
	straight-run diesel	10,100	130	2	4.43	92	293.43	

significant increase in the residual sulfur content to 4472 ppm is observed. This result is probably a consequence of the decrease in the selectivity of oxidation of sulfur-containing compounds due to the occurrence of side processes of oxidation of hydrocarbon components of the studied raw materials. In order to achieve a deeper degree of sulfur removal, a two-stage process of aerobic oxidative desulfurization was carried out. For this purpose, AODS of a diesel fuel sample was carried out, and after extraction with methanol and recovery of oxidation products, the same partially purified diesel fuel sample was repeatedly subjected to AODS with a fresh portion of catalyst under the same conditions. This approach made it possible to reduce the total sulfur content in the studied diesel fraction from 10,100 to 345 ppm, which corresponds to a desulfurization degree of 96.6%.

Table 3 lists the currently known catalysts for aerobic oxidative desulfurization containing molybdenum, tungsten or iron compounds as an active component. The data are presented taking into account the type of feedstock being purified, the total sulfur content, the conditions of the aerobic oxidation reaction, the conversion, and the specific catalytic activity, which is calculated as the ratio of moles of the reacted

sulfur-containing substrate per gram of catalyst per unit time. This indicator allows for unification of the results and better comparison of the efficiency of the known catalysts. It is important to note that most of the currently known catalysts for aerobic oxidative desulfurization were tested on model fuels, where there are no problems with side processes. This is one of the key challenges of AODS, because often the results obtained during the oxidation of model fuels cannot be applied to the desulfurization of real petroleum products, which significantly complicates the application of the obtained results in practice. In this work, the catalyst activity was tested both on a model mixture (to be able to compare the efficiency with known analogues) and on a real sample of straight-run diesel fraction with a high initial sulfur content of more than 1%.

Known AODS catalysts operate in approximately the same temperature range of 100-150 °C. At a lower temperature, it is not possible to activate atmospheric oxygen and reactions practically do not occur, and at higher temperatures than the specified range, side reactions of hydrocarbon oxidation are enhanced, which is an extremely undesirable process, leading to product losses.

According to the data in Table 3, the oxidation time, as a rule, is hours and varies in the range of 1-8 h. Such a long reaction time also complicates the practical application of the AODS process, since it significantly complicates the equipment design, allowing for long-term contact of the fuel with the oxidizer and catalyst. In this work, conditions are proposed under which it is possible to achieve complete conversion of DBT in just 20 min of oxidation. Specific catalytic activity varies from hundredths to tens of moles of converted substrate per gram of catalyst per unit time. Most catalysts demonstrate specific catalytic activity in the range of 0.5-10 mmol/(g h), while in the presence of the synthesized synergistic catalyst this value reaches 12 for the model mixture and 293 for the real diesel fraction. The high value for the diesel fraction is explained by the very high sulfur content in the purified feedstock.

Thus, the synthesized synergistic catalyst operates under conditions in which known catalysts are often tested, but its significant difference is the possibility of application for the real diesel fraction, as well as a significantly shorter reaction time.

4. CONCLUSIONS

Thus, in this work we have developed a new synergistic catalyst based on mixed carbides of iron, molybdenum and tungsten, which exhibits high efficiency both in the process of aerobic oxidation of model sulfur-containing substrates and in the process of aerobic oxidative desulfurization of a real sample of straight-run diesel fraction. In the work for the first time it was proposed to combine molybdenum and tungsten carbides for the oxidation process and it was shown in detail what advantages such an approach has in comparison with the use of single-phase carbides or simply oxides of transition metals. The synthesized catalysts were studied in detail by a set of physicochemical methods to determine the composition and structure of the obtained materials. It is important to note that the catalysts were synthesized using microwave radiation, which makes it possible to significantly reduce the reaction time for obtaining carbides to literally several minutes and at the same time significantly increase the energy efficiency of the entire synthesis process. According to the XRD results, the synthesized samples are predominantly a mixture of molybdenum and tungsten carbides, and also contain

reflections of lower intensity corresponding to the phases of mixed carbides and oxides of the corresponding metals. According to the TEM results, the carbide samples are nanosized particles with a narrow size distribution in the range of 10–20 nm. According to the XPS results, the surface of the carbide particles is largely covered with oxides of the corresponding transition metals due to oxidation of the carbides by atmospheric oxygen.

The synthesized FeMoWC catalysts with different molar ratios of molybdenum to tungsten were studied in detail in the process of aerobic oxidation of model fuel containing dibenzothiophene. It was shown that when using iron, molybdenum and tungsten in the catalyst composition, it is possible to achieve a synergistic effect, when the substrate conversion is significantly higher compared to mixed twocomponent carbides containing only iron with molybdenum or iron with tungsten. Thus, when switching from the FeMoWC 1/4 to FeMoWC 4/1, i.e. with an increase in the molybdenum content, a noticeable increase in DBT conversion from 60 to 77% was recorded, while in the presence of FeMoC catalyst (without tungsten) a significantly worse result in DBT conversion equal to 43% was obtained. According to the results of varying the catalyst dosage the higher the molybdenum content in the system, the higher the catalyst activity at lower dosages and the more sensitive the DBT conversion is to the excess of catalyst in the system, which can be explained with decomposition of alkyl peroxides. The same results were obtained during the tests with hydrogen peroxide decomposition according which the higher content of molybdenum in the catalyst leads to more intense decomposition of the peroxide. The catalyst allows achieving complete conversion of DBT in a wide temperature range from 100 to 150 °C. It was shown that at a temperature of 130 °C, it is possible to achieve complete oxidation of dibenzothiophene in 40 min of oxidation, and at 150 °C--in just 20 min. The work demonstrates for the first time the possibility of using mixed carbides for aerobic oxidative desulfurization of diesel fraction with a high initial sulfur content of more than 1%. Under the selected optimal conditions, the degree of desulfurization of the diesel fraction was 96.6%.

The approaches to the rapid synthesis of synergetic mixed carbides proposed in this paper make a significant contribution to the development of the aerobic oxidative desulfurization method, which can be used to produce motor fuels that meet strict environmental standards. The obtained results open up possibilities for further development of this topic, including by developing approaches to scaling up microwave synthesis, expanding the types of raw materials for purification, as well as further studies of the detailed mechanism of the process. The proposed approaches can be used for the widespread use of transition metal carbides in the development of energy-efficient oxidation processes using an environmentally friendly and accessible oxidant—atmospheric oxygen.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.4c06380.

XRD patterns of FeMoWC 1/4, FeMoWC 1/1, FeMoWC 4/1, FeMoC; XPS spectra and accounting for X-ray phase peaks of FeMoWC 1/4, FeMoWC 1/1,

FeMoWC 4/1; O_{ads}/O_{lat} ratios for catalysts; kinetic research; oxygen/sulfur molar ratios at different pressures (PDF)

AUTHOR INFORMATION

Corresponding Author

Argam Akopyan – Chemistry Department, Lomonosov Moscow State University, 119991 Moscow, Russias;
orcid.org/0000-0001-6386-0006; Email: arvchem@ yandex.ru

Authors

Artur Aghoyan – A.B. Nalbandyan Institute of Chemical Physics National Academy of Sciences of Armenia, 0014 Yerevan, Armenia; Orcid.org/0000-0001-9917-5457

Ekaterina A. Eseva – Chemistry Department, Lomonosov Moscow State University, 119991 Moscow, Russias; orcid.org/0000-0001-7538-9012

Maxim O. Lukashov – Chemistry Department, Lomonosov Moscow State University, 119991 Moscow, Russias; orcid.org/0000-0002-4656-6232

Mikhail M. Belov – Chemistry Department, Lomonosov Moscow State University, 119991 Moscow, Russias

Davit Davtyan – A.B. Nalbandyan Institute of Chemical Physics National Academy of Sciences of Armenia, 0014 Yerevan, Armenia; ⊚ orcid.org/0000-0002-6805-2793

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.energyfuels.4c06380

Author Contributions

All authors contributed equally. The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

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Notes

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