

Oxidative Desulfurization of Fuels Using Heterogeneous Catalysts Based on MCM-41

Polina Polikarpova,[†] Argam Akopyan,[†] Anastasia Shigapova,[†] Aleksandr Glotov,^{†,‡,✉}
Alexander Anisimov,^{*,†,✉} and Eduard Karakhanov[†]

[†]Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory 1–3, 119234 Moscow, Russia

[‡]Department of Physical and Colloid Chemistry, Gubkin University, 119991 Moscow, Russia

ABSTRACT: Mesoporous silicas of MCM-41 type modified by transition metal oxides, such as molybdenum, vanadium, and tungsten, were synthesized. These materials were characterized by low-temperature nitrogen adsorption/desorption, Fourier transform infrared spectroscopy, X-ray spectral fluorescence analysis, and transmission electron microscopy techniques and applied for the removal of sulfur compounds in model and real fuels by oxidative desulfurization. The catalysts obtained were tested under optimal conditions. Dibenzothiophene was removed completely, and sulfur removal in gasoline and diesel fractions could reach 91 and 63%, respectively. These catalysts retain their activity in gasoline fraction desulfurization for 5 cycles.

1. INTRODUCTION

According to ecological requirements, the sulfur content in motor fuels (gasoline and diesel) should not exceed 10 ppm.¹ Hydrodesulfurization (HDS), as one of the most common desulfurization method, requires high capital and energy costs for its implementation.^{2,3} HDS is effective for the removal of aliphatic sulfur compounds, such as thiols, thioethers, and disulfides, but is inefficient for removal of heterocyclic sulfur compounds, such as benzothiophene (BT), dibenzothiophene (DBT), and their alkyl derivatives.⁴ For this purpose, non-hydrogen desulfurization methods, such as oxidative desulfurization (ODS), adsorption, extraction, and biodesulfurization, have been recently developed.^{5–7} Among non-hydrogen methods of sulfur removal from fuels, ODS has become the most widespread method.^{4,8} This method is often used with subsequent extraction and adsorption of oxidation products.^{9–12} In contrast to HDS, ODS is performed under mild conditions (atmospheric pressure, lower temperatures, and without hydrogen), allowing for the reduction of capital costs.^{8,13}

In the ODS process, catalysts play an important role, because they are responsible for activation of oxidants.¹⁴ Salts of transition metals are widely used as catalysts for ODS, because they are capable of forming peroxo complexes.^{8,15} For ODS, there are known homogeneous and heterogeneous catalysts comprising transition metals.^{16,17} The main disadvantage of homogeneous catalysts is the complexity of their recovery and regeneration. Therefore, heterogeneous catalysts for ODS are increasingly developed. In the case of heterogeneous catalysts, the carrier plays an important role. It affects the catalyst activity, selectivity, and stability and provides a catalyst recovery from the reaction mixture.¹⁸

Mesoporous silicas, such as MCM-41, SBA-15, and others, are frequently used as the catalyst carriers.^{19–21} Mesoporous materials have the following features: high specific surface area (up to 1000 m²/g) and narrow size distribution of wide pores (~4 nm), wherein a steric hindrance for adsorption of bulky sulfur-containing molecules (for example, alkylidibenzothio-

phenes) is absent.^{22,23} In general, the ODS catalysts are polyoxometallates or oxides of molybdenum and tungsten supported on MCM-41,^{24,25} but titanium, iron, and nickel are used scarcely.^{26,27} Using these catalysts, model sulfides are oxidized completely.^{28,29}

The purpose of this study is to investigate the activity of catalysts based on molybdenum, tungsten, and vanadium oxides supported on mesoporous silica MCM-41 type in oxidation of model and real fuels.

2. EXPERIMENTAL SECTION

2.1. Materials and Reagents. In this work, a straight-run gasoline fraction with a total sulfur content of 730 ppm and a diesel fraction with a total sulfur content of 2050 ppm were used as feedstock.

The model mixture consisted of 1000 ppm of DBT (98%, Sigma-Aldrich) in dodecane (99%, Sigma-Aldrich). Model mixtures containing methylphenylsulfide (MeSPh, 99%, Acros Organics) and BT (98%, Sigma-Aldrich) were prepared similarly.

The following reagents were used in the work: (NH₄)₂MoO₄, (NH₄)₄W₃O₁₇·2.5H₂O, NH₄VO₃, hydrogen peroxide (50 wt %) from Prime Chemicals Group, cetyltrimethylammonium bromide (CTAB, 98%) from Sigma-Aldrich, tetraethoxysilane (TEOS, 98%) from Acros Organics, and ammonia (25%) from Sigma-Tech.

2.2. Synthesis of Catalysts and Their Characterization. Mesoporous silica of MCM-41 type was synthesized by the following procedure:³⁰ CTAB (9.026 g) was dissolved in distilled water (424 mL); 25% ammonia (34.87 mL) was added to the resulting mixture under stirring; and the mixture obtained was stirred for 30 min at 30 °C. TEOS (37.2 mL, 0.16 mol) was added dropwise to the resulting mixture for 30 min and then stirred at room temperature for 4 h. The resulting gel was allowed to stand for 24 h at room temperature. The gel obtained had the following composition: 6.7SiO₂/CTAB/18NH₃/995H₂O. The mesoporous silica obtained was dried, heated (5 °C/min) to 550 °C, and calcined in air flow for 5 h.

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Modification of MCM-41 was performed by impregnation with a solution of $(\text{NH}_4)_2\text{MoO}_4$, $(\text{NH}_4)_4\text{W}_5\text{O}_{17}\cdot 2.5\text{H}_2\text{O}$, and NH_4VO_3 in distilled water. Then, 1 g of MCM-41 was immersed in a precursor solution for 30 min for aging and held for 24 h at 80 °C to remove water. The catalysts were then heated (5 °C/min) to 500 °C and calcined for 5 h.

Fourier transform infrared (FTIR) spectra were recorded in KBr tablets on a Nicolet IR200 FTIR spectrometer in the range of 500–4000 cm^{-1} .

An investigation of the elemental composition by X-ray spectral fluorescence analysis (RSFA) was carried out on an X-ray fluorescence wave spectrometer ARL PERFORM^X (Thermo Fisher Scientific, New Wave).

The characteristics of the porous structure of samples were determined on a Micromeritics Gemini VII 2390 (V1.02 t) analyzer according to the standard procedure. Before analysis, samples were evacuated at 350 °C for 12 h to a pressure of 3×10^{-3} atm. The nitrogen adsorption–desorption isotherm was measured at 77 K. The features of the porous structure were calculated using standard software. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) model in the range of relative pressures $P/P_0 = 0.05$ – 0.30 . The total pore volume was calculated by the Barrett–Joyner–Halenda (BJH) model at a relative pressure of $P/P_0 = 0.95$.

2.3. Experimental and Analytical Methods. The oxidation reactions with DBT model mixtures were carried out according to the following procedure: 0.5–2 wt % of the catalyst and 0.006–0.06 mL of hydrogen peroxide were added to the 5 mL solution of DBT, and oxidation time varied from 0.5 to 6 h in a temperature range of 20–80 °C. During the experiments, the following conditions were varied: reaction time, oxidation temperature, and amounts of hydrogen peroxide and catalyst.

The control of the reaction product composition and the purity of the starting materials was performed by gas chromatography using a Crystal-2000M set (flame ionization detector; column, Zebron; L , 30 m; d , 0.32 mm; liquid phase, ZB-1) while programming the temperature from 100 to 250 °C (the carrier gas is helium). Chromatograms were recorded and analyzed using the Chromatech Analytic 1.5 program.

Oxidation of fuels was performed by the following procedure: 0.03–0.24 g of the catalyst and 0.01–0.08 mL of hydrogen peroxide were added to 15 mL of fuel. The reaction was carried out for 0.5–6 h in the temperature range of 20–80 °C. During the experiments, the following conditions were varied: reaction time, oxidation temperature, amount of hydrogen peroxide, amount of the catalyst, and nature of the catalyst.

After oxidation, the reaction mixture was passed through silica gel to remove the oxidized products.

The total sulfur content in hydrocarbon fractions was determined using a sulfur analyzer ASE-2 (analyzer of sulfur energy dispersion) according to the ASTM D4294-10 standard.³¹ The method is based on X-ray fluorescence energy-dispersive spectrometry to determine the sulfur mass fraction in diesel and unleaded gasoline in the range from 7 to 50 000 ppm with a relative error of 3%.

Each experiment was made repeatedly to obtain a minimum of three convergent results, which differ from the average value less than 5%. The average values were reported in Figures 4–9. The measurement error is less than 5%.

3. RESULTS AND DISCUSSION

3.1. Characterization of MCM-41 and the Me–MCM-41 Catalyst. Characterization of the support and catalysts was performed to study the features of the synthesized catalysts.

The obtained catalysts were characterized by FTIR (Figure 1). As shown by infrared (IR) spectra of MCM-41, the intensity of the Si–O–H peaks decreases for modified samples, indicating that the surface of material is screened with metal oxides.

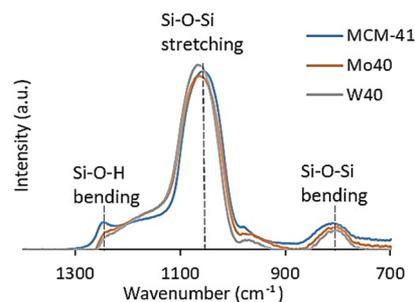


Figure 1. FTIR spectra of Mo–MCM-41, W–MCM-41, and MCM-41.

Elemental analysis of catalysts obtained is shown in Table 1. Analysis showed that impurities of other metals are absent in the prepared catalysts. Data in the table show that composition of catalysts obtained is in agreement with that calculated. The catalyst designations used in the paper are also given in Table 1.

N_2 adsorption–desorption isotherms of MCM-41, Mo40–MCM-41, and W40–MCM-41 are depicted (Figure 2). The N_2 isotherms of all samples are of type IV. The N_2 isotherms of samples have a capillary condensation step in the range of partial pressures between 0.4 and 0.8 that indicates the presence of a mesoporous framework. The shape of the isotherms of both W40 and Mo40 catalysts is similar to that of the MCM-41 carrier, indicating that the porous characteristics of the support have not been damaged after metal loading followed by calcination. Experimental parameters were listed in Table 2.

The morphology of samples before and after the oxidation reaction is shown in Figure 3. As shown by TEM images, W40–MCM-41 before and after the oxidation reaction exhibited a similar structure, which provided strong evidence that the mesoporous structure of the support was retained after oxidation in the presence of hydrogen peroxide. The particle size distribution of W40 is shown in Figure 3.

3.2. Oxidation of Model Sulfides. **3.2.1. Effect of the Oxidation Temperature.** Catalytic activity of the catalysts obtained was studied on a model mixture of DBT, BT, and MeSPH in dodecane. The oxidation reaction of DBT proceeds as shown in Scheme 1.

The oxidation product of DBT is the corresponding sulfone, which is confirmed by gas chromatography.

The oxidation of DBT was performed at various operating temperatures. Me40–MCM-41 were used as the catalyst in the oxidation reaction. An investigation of the effect of the temperature on the oxidation conversion of DBT showed that the optimal oxidation temperature is 60 °C (Figure 4a).

Figure 4a also shows that V40–MCM-41 is not an effective catalyst for oxidation reactions of DBT; therefore, its further study was excluded.

3.2.2. Effect of the Metal Content. The effect of the quantity of metal (molar ratio of Mo/MCM-41) on oxidative conversion of DBT was investigated with different contents of molybdenum and tungsten (from 1:320 to 1:20) on the MCM-41 framework. It can be seen from Figure 4b that catalysts with a molar ratio Me/MCM-41 = 1:80 and higher are effective in DBT oxidation.

3.2.3. Effect of the Oxidant/Sulfur (O/S) Molar Ratio. Figure 5a shows the dependence of the oxidation conversion of DBT upon the amount of hydrogen peroxide. Experiments

Table 1. Elemental Analysis of the Catalysts Obtained

MCM-41/Me (M)	theoretical amount of metal (wt %)			experimental amount of metal (wt %)			designation
	Mo	W	V	Mo	W	V	
40	3.53	3.42	1.88	2.21	2.90	1.46	Me40
80	1.76	1.71	0.94	1.50	0.97	0.87	Me80
160	0.88	0.85	0.47	0.73	0.51	0.38	Me160

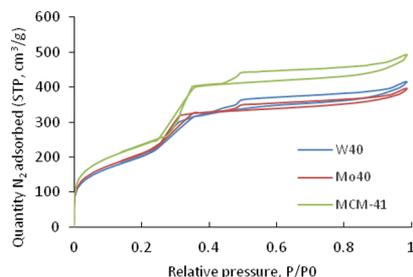


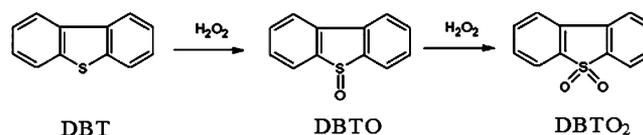
Figure 2. Nitrogen adsorption-desorption isotherms of obtained catalysts.

Table 2. Textural Properties of Various Samples

sample	BET surface area (m ² /g)	pore volume (cm ³ /g)	pore size (Å)
W40	763	0.64	24
W40 after reaction	722	0.59	28
Mo40	780	0.61	23
MCM-41	846	0.75	22

were performed at different H₂O₂/S molar ratios in the range of 2:1–10:1. A 4-fold excess of hydrogen peroxide is sufficient for complete oxidation of DBT using catalysts with the molar ratio Me/MCM-41 = 1:40. The Mo80 catalyst is active only with a large excess of hydrogen peroxide. In this case, the W80 catalyst exhibits high activity with a double excess of hydrogen

Scheme 1. Oxidation Reaction of DBT



peroxide. For Mo40 and W40 catalysts, full oxidation of DBT is achieved with a 4-fold excess of peroxide.

3.2.4. Effect of the Catalyst Amount. The effect of the catalyst amount on the conversion of DBT oxidation was studied for 0.5–2 wt % (Figure 5b). It is shown that the optimal amount of the catalyst is 1 wt %, where the complete conversion of DBT was observed. For 2 wt % W40, the conversion decreases, which may be connected with hydrogen peroxide decomposition by an excess of the catalyst.

3.2.5. Effect of the Reaction Time. The dependence of sulfide oxidation upon time is shown in Figure 6. As seen from the figure, the activity of sulfides falls in the following order: MeSPH > DBT > BT. The complete oxidation of MeSPH, BT, and DBT was achieved in 1, 6, and 2 h, respectively.

3.3. Desulfurization of Fuels. Oxidation of DBT shows that the catalysts with a ratio MCM-41/Me = 40:1 are most effective in this reaction. Activities of these catalysts were investigated in oxidation of gasoline (total sulfur content of 730 ppm) and diesel fractions (total sulfur content of 2050 ppm). After oxidation, the reaction mixture was passed

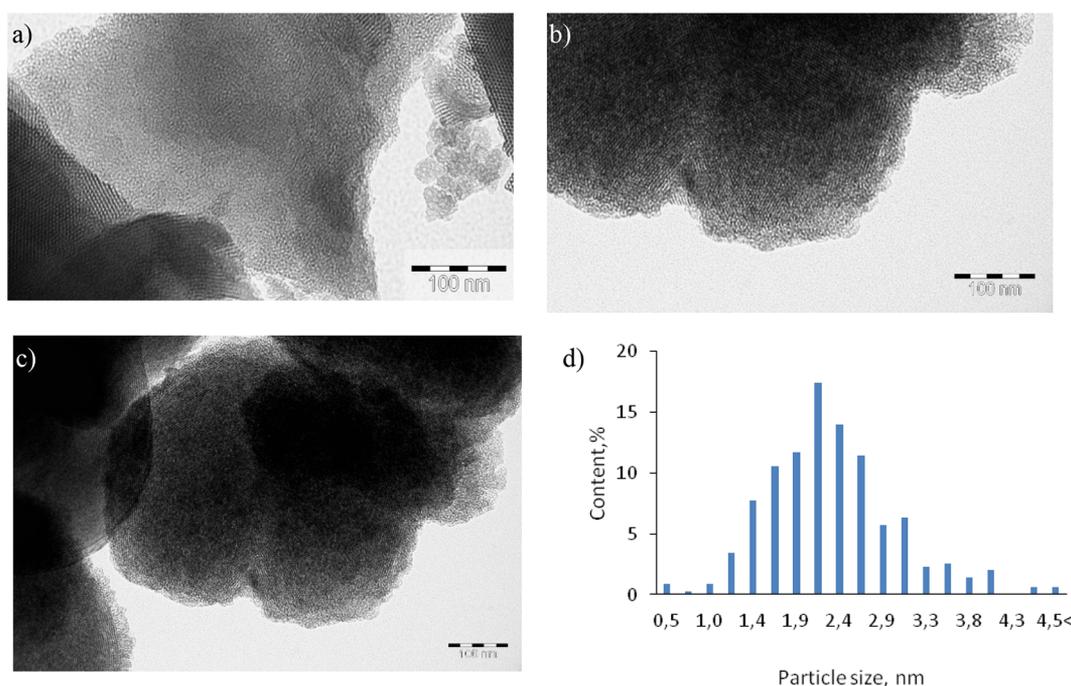


Figure 3. (a–c) TEM images of obtained catalysts and (d) distribution of the particle size in W40–MCM-41: (a) MCM-41, (b) W40–MCM-41 before the oxidation reaction, and (c) W40–MCM-41 after the oxidation reaction.

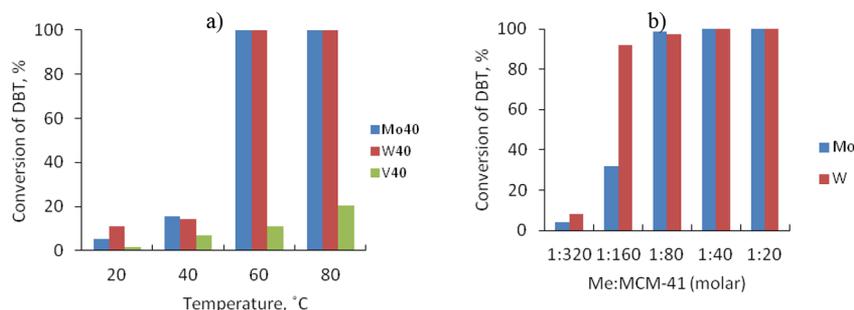


Figure 4. Effect of the (a) temperature and (b) amount of metal in 1 wt % catalyst on the conversion of DBT. Oxidation conditions: (a) $\text{H}_2\text{O}_2/\text{S} = 10:1$ and 2 h and (b) $\text{H}_2\text{O}_2/\text{S} = 10:1$, 2 h, and 60 °C.

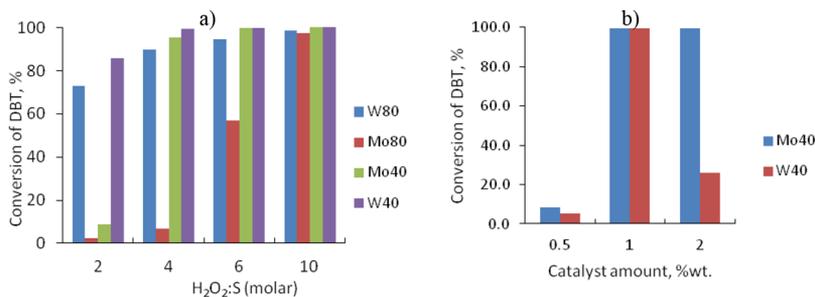


Figure 5. Effect of the (a) oxidant/sulfur molar ratio ($\text{H}_2\text{O}_2/\text{S}$) and (b) catalyst amount on the conversion of DBT. Oxidation conditions: (a) 1 wt % catalyst, 60 °C, and 2 h and (b) $\text{H}_2\text{O}_2/\text{S} = 4:1$, 2 h, and 60 °C.

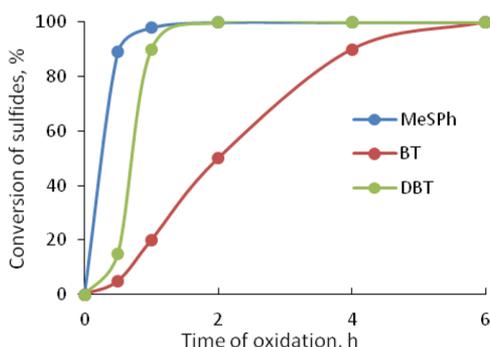


Figure 6. Effect of the reaction time on the oxidation of sulfides. Oxidation conditions: 1 wt % W40, $\text{H}_2\text{O}_2/\text{S} = 4:1$, and 60 °C.

through the silica to remove oxidized sulfur compounds. Because of the high content of hardly oxidized sulfur compounds in the diesel fraction, in this case, less of a decrease in total sulfur is observed in comparison to the gasoline fraction.

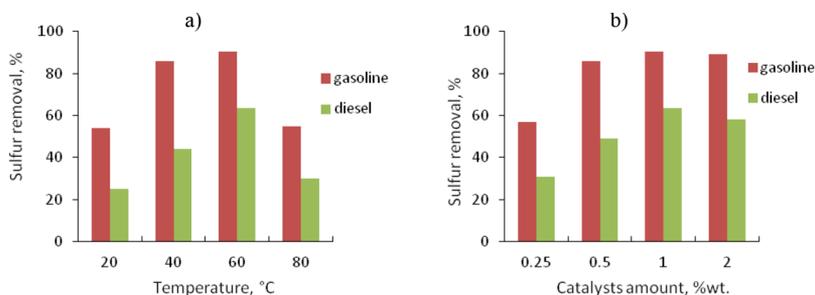


Figure 7. Effect of the (a) temperature and (b) catalyst amount on the desulfurization of gasoline and diesel fractions. Oxidation conditions: (a) 1 wt % catalyst, $\text{H}_2\text{O}_2/\text{S} = 6:1$, and 2 h and (b) $\text{H}_2\text{O}_2/\text{S} = 6:1$, 2 h, and 60 °C.

3.3.1. Effect of the Desulfurization Temperature. To study the effect of the temperature on the conversion of sulfur compounds in real fuels, oxidation reactions were performed at 20, 40, 60, and 80 °C (Figure 7a).

As seen from Figure 7a, the desulfurization conversion increases with a rising temperature from 20 to 60 °C but falls as the temperature reaches 80 °C, which may be connected with the hydrogen peroxide decomposition.

3.3.2. Effect of the Catalyst Amount. To study the effect of the catalyst amount on the conversion of sulfur compounds in fuels, the W40 sample was used in concentrations of 0.25, 0.5, 1, 2 wt % based on the feed (Figure 7b). The best results were obtained in experiments with 1 wt % of the catalyst. The slight decrease in conversion with an increasing amount of the catalyst may be connected with the decomposition of hydrogen peroxide.

3.3.3. Effect of the O/S Molar Ratio. An investigation of the effect of hydrogen peroxide amounts on the conversion of sulfur compounds in fuels was carried out using the W40 catalyst. The experiments were performed at 60 °C for 2 h. As shown by results in Figure 8a, a 4-fold excess of oxidant is

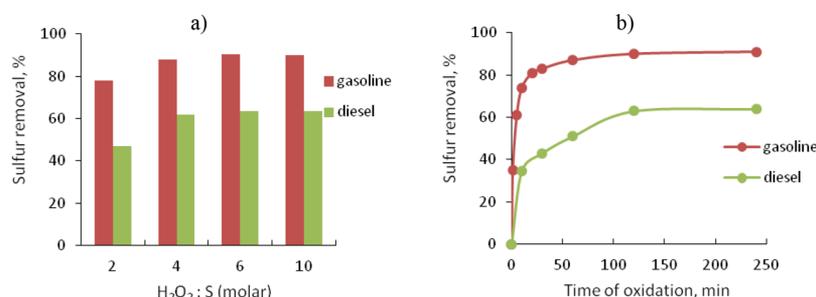


Figure 8. Effect of the (a) oxidant/sulfur molar ratio ($\text{H}_2\text{O}_2/\text{S}$) and (b) reaction time on the desulfurization of gasoline and diesel fractions with 1 wt % catalyst. Oxidation conditions: (a) 60 °C and 2 h and (b) $\text{H}_2\text{O}_2/\text{S} = 6:1$ and 60 °C.

sufficient to reach the maximal desulfurization of gasoline and diesel fractions.

3.3.4. Effect of the Reaction Time. The kinetics of the desulfurization of gasoline and diesel fractions was studied in the presence of the catalyst W40 (Figure 8b). Within 30 min of the oxidation, the maximal desulfurization of the gasoline fraction was achieved. For the diesel fraction, the optimal desulfurization time is 2 h.

3.4. Reusability of Catalysts. For the gasoline fraction, reusability of catalyst W40 was performed at optimal operating conditions. After oxidation, the catalyst was washed with acetone at room temperature to desorb sulfur compounds. Subsequently, the purified catalyst was dried at the temperature of 80 °C for 4 h, and the regenerated catalyst was reused for the next cycle. Figure 9 depicts the reusability of the

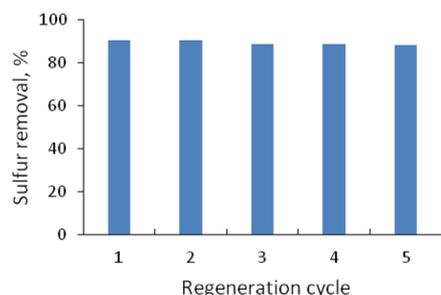


Figure 9. Regeneration ability of the W40–MCM-41 catalyst at optimal operation conditions (1 wt % catalyst, $\text{H}_2\text{O}_2/\text{S} = 6:1$, 60 °C, and 2 h).

catalyst; it is concluded that the desulfurization extent of the gasoline fraction decreases from 90.4 to 88.4% in 5 cycles. This decrease may be connected with some error of the experiments.

4. CONCLUSION

Molybdenum, tungsten, and vanadium mesoporous catalysts were prepared. The obtained catalysts were characterized by nitrogen adsorption/desorption, FTIR, and RSFA. Mo–MCM-41 and W–MCM-41 catalysts proved to be very effective for the oxidation of sulfur compounds in model and real fuels using hydrogen peroxide as an oxidant. Optimal oxidation conditions for DBT are as follows: $\text{H}_2\text{O}_2/\text{S}$ (M) of 4:1, W40–MCM-41 amount of 1 wt %, temperature of 60 °C, and process duration of 1 h. Optimal oxidation conditions for real fuels are as follows: $\text{H}_2\text{O}_2/\text{S}$ (M) of 4:1, W40–MCM-41 amount of 1 wt %, temperature of 60 °C, and process duration of 2 h. The applied catalyst was easy to regenerate and showed stable performance after 5 cycles.

AUTHOR INFORMATION

Corresponding Author

*Telephone: +7-495-939-53-77. E-mail: sulfur45@mail.ru.

ORCID

Aleksandr Glotov: 0000-0002-2877-0395

Alexander Anisimov: 0000-0001-9272-2913

Notes

The authors declare no competing financial interest.

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