

Catalysts Based on Acidic SBA-15 for Deep Oxidative Desulfurization of Model Fuels

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ABSTRACT: Acidic SBA-15 modified by molybdenum oxide has been synthesized. These materials were characterized by low nitrogen adsorption/desorption, Fourier transform infrared spectroscopy, transmission electron microscopy, NH₃ temperature-programmed desorption, NMR, and XRD techniques. In this work, the activity of acidic Al-SBA-15 modified with molybdenum oxide in the oxidation of sulfur-containing compounds was investigated for the first time. It was shown that the SBA-15 support containing aluminum allows to significantly increase the catalytic activity of molybdenum oxide. The main factors affecting the process consisting of catalyst dosage, temperature, reaction time, oxidant dosage were investigated in detail. In the presence of synthesized catalysts, dibenzothiophene can be completely oxidized in 30 min. These catalysts retain their activity in DBT oxidation for 10 cycles.

1. INTRODUCTION

In recent years, the trend of using molecular sieves in research and industries grows at an exponential rate. In particular, mesoporous supports with pore diameters from 2 to 50 nm were investigated in detail. Such materials are widely used as adsorbents, catalysts, and supports because of their large surface area, large pore volumes, and well-ordered structure.¹ Among the class of mesoporous silica, SBA-15 is one of the most widely used materials. Unlike MCM-41, it has larger pores and stronger pore walls.²

This material SBA-15 was investigated in detail as a support for heterogeneous oxidative desulfurization catalysts.³ This is because of several factors: optimal pore size for the oxidation of sulfur-containing substrates, ease of modification, and stability under oxidation conditions.^{4,5} Oxidative desulfurization is an alternative method for removing sulfur from fuels.^{6–9} The increase of average sulfur content in extracted petroleum and also the increase of condensed dibenzothiophene (DBT) derivatives content in petroleum distillates lead to an increase in the cost of the hydrodesulfurization process because of the increase of temperature, pressure, and catalyst deactivation.^{6,10,11} In this regard, alternative desulfurization methods can act at a pretreatment stage or after hydrodesulfurization. Both of these ways are possible because nonhydrogen desulfurization methods allow removal of sulfur-containing components that do not react under hydrodesulfurization conditions.^{11,12}

Currently, there are four main nonhydrogen desulfurization methods: adsorption, extraction, oxidative desulfurization, and biodesulfurization.^{13–17} Among these methods, the most developed is the oxidative desulfurization because this method allows to reduce the content of sulfur in petroleum distillates by more than 99%, without affecting the hydrocarbon part.^{7,18,19}

Transition-metal oxides are the most widely used catalysts for oxidative desulfurization.^{20–22} Such catalysts are obtained by applying metal salt to the support, followed by calcination.^{23,24} In this case, zeolites, mesoporous materials, and polymer matrices are used as supports.^{25–34} However, because of the pore size from 2 to 50 nm, supports based on SBA-15 are becoming more widespread.^{3,35} Currently, there are known catalytic systems based on SBA-15 containing oxides of tungsten, molybdenum, and vanadium as catalysts for the oxidation of DBT.³ However, in the presence of such catalysts, oxidation takes quite a long time (on average, 2 h). It is known that oxidation of sulfur compounds is faster in an acidic environment;^{7,36} therefore, the direction for the synthesis of catalysts based on SBA-15 which contains phosphomolybdate and phosphotungstate acid is developing.^{3,37,38}

The disadvantage of such catalysts is their high cost; in this regard, the possibility of accelerating the oxidation of DBT by increasing the acidity of support was first studied in this paper. Besides, a comparison of molybdenum-containing catalysts with different acidity is also made. It is important to note that no articles on oxidative desulfurization that make use of aluminum-containing SBA-15 as a support have been published so far.

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2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. The mesoporous support SBA-15 was prepared according to the following procedures. First, under stirring, 12.9 g of Pluronic P123 was dissolved in 486 mL of 1.6 M hydrochloric acid solution at 30 °C. Second, the temperature of the reaction mixture was raised to 40 °C, and then, 34.72 g of TEOS was added drop by drop for 2 h. After mixing at 40 °C for 24 h, the mixture was transferred to an autoclave and kept at 100 °C for 24 h. Then, the white precipitate was washed with distilled water, filtered, and dried in the temperature range of 80–110 °C. The final SBA-15 was obtained by calcining the precipitate at 550 °C for 5 h at a heating rate of 5 °C/min.³⁹

The synthesis of Al-SBA-15 was performed according to the method presented in ref 40. A total of 10 g of SBA-15 (0.1666 mol) and 0.68 g of aluminum isopropoxide (0.00325 mol) were dissolved in 400 mL of hydrochloric acid (0.075 M) at room temperature. The resulting mixture was mixed for 15 h. Then, the mixture was filtered, dried for 4 h at 80 °C and 4 h at 90 °C, and then calcined for 2 h at 300 °C and 4 h at 550 °C.

Modification of SBA-15 and Al-SBA-15 was performed by impregnation with a solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ and $\text{H}_7\text{PMo}_{12}\text{O}_{42}$ (HPMo) in distilled water. A total of 1 g of the support was placed in a solution of salt (or acid) at 60 °C with constant stirring for 2 h. Then, the resulting catalyst was dried for 24 h at 80 °C to remove water. Then, catalysts were heated (5 °C/min) to 500 °C and calcined for 5 h.

2.2. Characterizations. Fourier transform infrared (FTIR) spectra were recorded in KBr tablets on a Nicolet Ir 200 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 sample weight (0.3 g) was ground until a homogeneous mass was obtained and then pressed on a boric acid substrate. The analysis was performed at atmospheric pressure.

The characteristics of the porous structure of the samples were determined on a Micromeritics Gemini VII 2390 (V1.02 t) analyzer according to the following procedure. Before analysis, the samples were evacuated at 350 °C for 12 h to a pressure of 3×10^{-3} atm. Nitrogen adsorption–desorption isotherms were performed at 77 K. The characteristics of the porous structure were studied using standard software. The specific surface area was calculated from the BET model (Brunauer–Emmett–Teller) at a relative partial pressure of $P/P_0 = 0.2$. The total pore volume was calculated from the BJH (Barrett–Joyner–Halenda) model at a relative pressure of $P/P_0 = 0.95$.

Transmission electron microscopy (TEM) was performed on a JEM-2100 (JEOL, Japan) microscope with an electron tube voltage of 200 kV.

X-ray analysis was carried out on a Rigaku Rotaflex D/max-RC instrument with Cu $K\alpha$ radiation ($\lambda = 0.154$ nm). The diffraction pattern of the sample was recorded at angles $2\theta = 3$ – 50° with a step of 0.04° at a scanning rate of 4°min^{-1} . The degree of crystallinity was calculated from the ratio between the areas (integral intensities) of peaks associated with the crystalline and amorphous phases.

²⁷Al MAS NMR experiments were performed on a Bruker AVANCE-II 400 spectrometer (9.4 T, $\nu^{27}\text{Al} = 104.3$ MHz). For recording ²⁷Al MAS NMR spectra, a 4 mm HX MAS probe was used with a spinning rate of 12 kHz. For all spectra, one-pulse sequence was used.

²⁷Al MAS NMR spectra were recorded with a 15° pulse length of 0.5 μs , a recycle delay of 0.5 s, and several scans of 8192. The chemical shifts were referenced to $\text{Al}(\text{NO}_3)_3$ (0 ppm).

The acidity of materials synthesized was determined by the ammonia temperature-programmed desorption method (NH_3 -TPD) performed on the AutoChem HP2950 instrument (Micromeritics, USA). The test sample of ~ 0.1 g with a particle size of 150–500 μ was inserted in a quartz reactor and treated in a flow of nitrogen at 500 °C for 1 h. Saturation was performed in a flow of dried ammonia

diluted with nitrogen at the temperature of 60 °C for 30 min. Physically adsorbed NH_3 was removed at 100 °C in a nitrogen flow of 30 mL/min for 1 h, followed by cooling to 60 °C. To obtain a TPD curve, the temperature was gradually increased to 800 °C at a rate of 10 °C/min.

2.3. Activity Assessment. The oxidation of model mixtures was carried out according to the following procedure: to 5 mL of a model mixture of sulfur compounds in dodecane, 0.00375–0.185 g of a heterogeneous catalyst and 0.007–0.02 mL of hydrogen peroxide were added. Oxidation was performed for 30–120 min at a temperature of 20–80 °C.

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.

Each experiment was carried out repeatedly to obtain a minimum of three convergent results, which differ from the average value by less than 5%. The average values are reported in Figures 5–8. The measurement error was less than 5%. After the reaction, the model mixture was weighed. The mass loss for all experiments was no more than 1%.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Support and Catalyst.

Characterization of the support and catalysts was performed to study the features of the synthesized catalysts. In this study, two supports for oxidative desulfurization catalysts were used: SBA-15 and Al-SBA-15 (Si/Al = 100, the weight content of aluminum is 1.0%). Molybdenum oxide from 5 to 7 wt % was applied to these supports, and the support SBA-15 was impregnated with phosphomolybdic acid (the amount of molybdenum is 7 wt %). Low-temperature nitrogen adsorption/desorption was performed for the synthesized supports SBA-15 and Al-SBA-15 and catalysts (Table 1 and Figure 1a).

Table 1. Experimental Parameters of Obtained Catalysts and Supports

sample	quantity of metal, % wt		textural properties		
	Al	Mo	BET surface area (m^2/g)	pore volume (cm^3/g)	pore size (Å)
SBA-15			521	0.53	44
5% Mo/SBA-15		5.5	481	0.52	44
7% Mo/SBA-15		7.3	459	0.50	43
HPMo/SBA-15		6.9	305	0.40	37
Al-SBA-15	1.2		465	0.41	46
5% Mo/Al-SBA-15	1.1	5.2	398	0.41	44
7% Mo/Al-SBA-15	1.1	7.0	357	0.40	43
7% Mo/Al-SBA-15 after 10 cycles of oxidation	1.1	6.8	341	0.40	44

The N_2 isotherms of all samples are related to type IV. The N_2 isotherms of obtained supports and catalysts 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 catalyst of the N_2 isotherm is similar to the support of the N_2 isotherm, which shows that the metal deposition process does not affect the texture characteristics of the catalyst. The experimental parameters are listed in Table 1. Table 1 also shows the elemental analysis of catalysts.

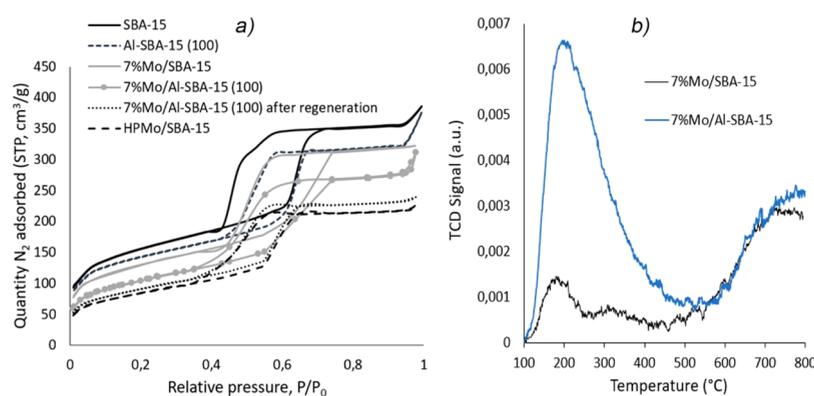


Figure 1. (a) Nitrogen adsorption–desorption isotherms of obtained supports and catalysts; (b) TPD profiles of NH₃ for catalysts containing molybdenum oxide.

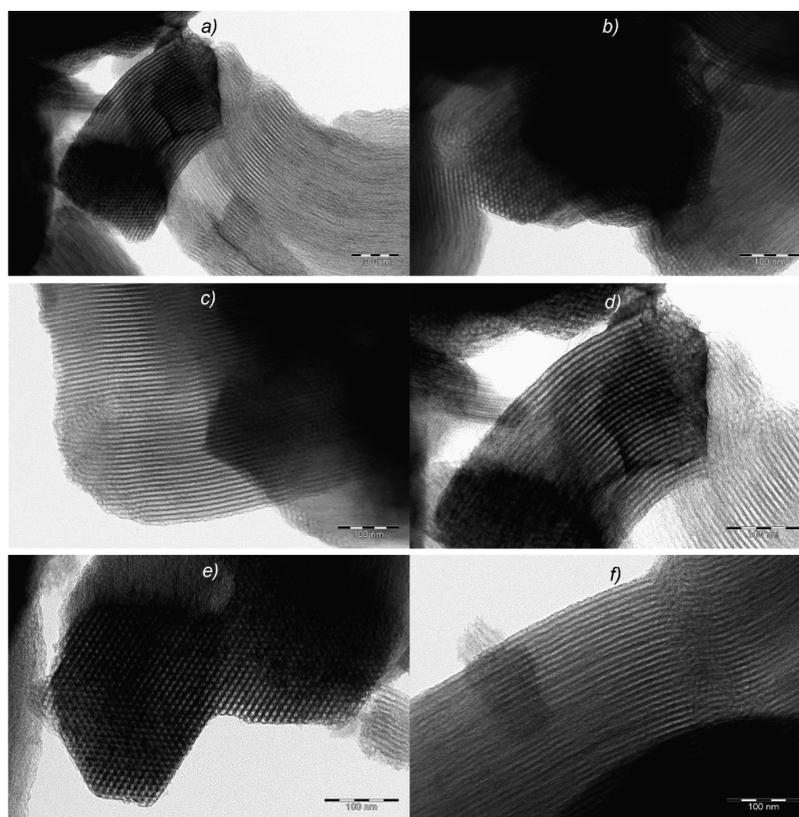


Figure 2. TEM images of obtained supports and catalysts: (a) SBA-15, (b) Al-SBA-15, (c) 7% Mo/SBA-15, (d) HPMo/SBA-15, (e) 7% Mo/Al-SBA-15 before the oxidation reaction, and (f) 7% Mo/Al-SBA-15 after the oxidation reaction.

Elemental analysis was performed using the RSFA method. The experimental amount of metals is slightly higher than the theoretical amount because the modification took a 5% excess of the metal precursor. The addition of molybdenum oxide leads to a slight decrease in the surface area and pore size because of pore filling. It should also be noted that among synthesized catalysts, HPMo/SBA-15 has the least surface area and pore size because of large size of the phosphomolybdic acid molecule in comparison with molybdenum oxide. For regenerated 7% Mo/Al-SBA-15 after 10 cycles of oxidation–regeneration, surface area and pore size are comparable with the initial catalyst, which indicates that oxidation and regeneration properties do not affect the catalyst structure. Elemental analysis of the spent catalyst shows that no

significant leaching of catalyst-active sites occur after oxidation and regeneration by acetone wash.

It is important to note that the introduction of 1% by mass aluminum in the structure of the support can increase its acidity from 0.384 to 0.431 mmol NH₃/g (Figure 1a). Acid centers of the support contribute to the acceleration of the oxidation reaction by the coordination of sulfur-containing compounds, which are Lewis bases. The thermal desorption curves have pronounced maxima around 190 °C corresponding to weak acid centers and maxima at 750 °C corresponding to strong acid centers. Catalyst 7% Mo/Al-SBA-15 contains much more weak acid centers in comparison with 7% Mo/SBA-15, which can explain the differences in the catalytic activity of these two catalysts.

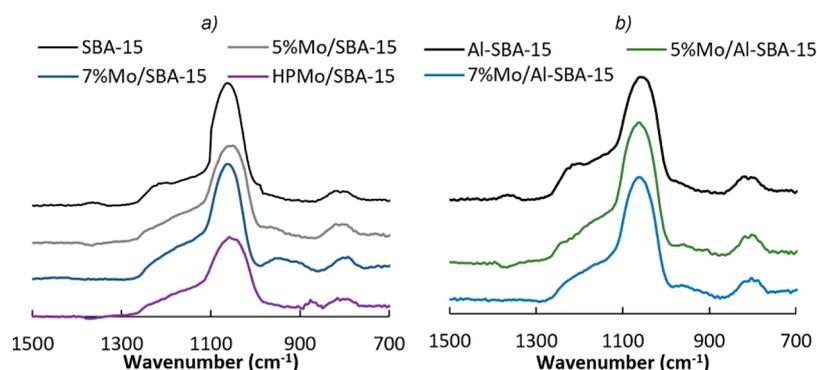


Figure 3. FTIR spectra of catalysts on SBA-15 (a) and catalysts on Al-SBA-15 (b).

TEM analysis of obtained catalysts (Figure 2) shows that all the samples obtained have a well-ordered hexagonal structure and parallel channels. The support Al-SBA-15 maintains the hexagonal structure of SBA-15, and the addition of molybdenum oxide and phosphomolybdic acid does not affect the initial SBA-15 structure. It should also be noted that this structure does not change for the spent catalyst after 10 cycles of oxidation–regeneration (Figure 2f).

The obtained catalysts were characterized by FTIR. As is shown in Figure 3, the infrared-peaks at 1086 and 805 cm⁻¹ were assigned to the asymmetric and symmetric stretching vibration of Si–O–Si, respectively.⁴¹ The other peak at 878 cm⁻¹ was supposed to be the bands for Mo–O–Mo of HPMo.⁴² The intensity of the Si–O–H (1240 cm⁻¹) peaks decreases for modified samples, indicating that the surface of the material is screened with metal oxides.

The support containing aluminum was also studied by solid-phase NMR spectroscopy (Figure 4).

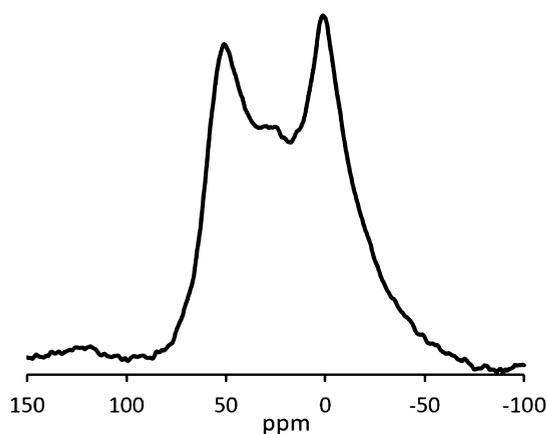


Figure 4. NMR spectrum of Al-SBA-15 (100).

The spectrum of the sample shows peaks responsible for the tetra- (51.7) and octahedral (−0.7) environment of aluminum, which is consistent with the structure of aluminum-containing SBA-15.⁴³ The appearance of a band in the region of 25–30 ppm indicates the presence of pentacoordinate Al.⁴⁴ The tetrahedral environment explains the presence of strong Brønsted acid centers in this support, and the presence of an octahedral environment explains the acid centers.⁴⁵

3.2. Oxidation of Model Sulfides. The activity of the catalysts obtained was studied on a model mixture of DBT in dodecane with an initial sulfur content of 500 ppm. The

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

As can be seen from Figure 5a, at a catalyst dosage of 0.5%, there is no difference between the 7% Mo-SBA-15 and 7% Mo–Al-SBA-15 catalysts because in both cases, the conversion reaches 100%. At a high catalyst dosage (0.5% by weight), the number of active sites in the form of molybdenum peroxy complexes is sufficient for complete oxidation of DBT. The difference between the catalysts becomes noticeable in Figure 5b, where their dosage is halved. Under these conditions, the role of aluminum is visible because it contributes to the acceleration of oxidation. This is because of the fact that the introduction of aluminum into the composition of the support increases its acidity and, thus, contributes to DBT coordination, which is the Lewis base. Thus, the introduction of acid sites into the support makes it possible to achieve complete oxidation of DBT at lower dosages of the catalyst with significant increase in its activity.

Further research was carried out in the presence of two catalysts: HPMo/SBA-15 and 7% Mo/Al-SBA-15.

The effect of the amount of hydrogen peroxide on DBT conversion is shown in Figure 6a. Hydrogen peroxide was chosen as the oxidant because water is the only byproduct of the reaction. Theoretically, a twofold excess of hydrogen peroxide is required for the complete reaction to occur. However, complete oxidation of DBT in 30 min in the presence of synthesized catalysts is observed with a fivefold excess of the oxidant. An increase in the hydrogen peroxide:sulfur ratio above 4:1 does not lead to a significant increase in conversion. This fact is related to the fact that, under these conditions, all active sites of the catalyst are involved in the formation of the peroxy complex, and the reaction rate can be limited by the desorption of the resulting reaction products—sulfones; therefore, the addition of an excess amount of the oxidant does not lead to an increase in conversion.

Varying the reaction temperature shows (Figure 6b) that an increase in temperature contributes to an increase in DBT conversion. An increase in temperature allows not only to increase the reactivity of DBT but also increases the rate of desorption of the reaction product—DBT sulfone from the catalyst surface (sulfones are well adsorbed on the catalyst surface because of the formation of hydrogen bonds⁴⁶). However, the possible decomposition of hydrogen peroxide is observed at 80 °C. In this regard, further catalytic experiments were carried out at a temperature of 60 °C.

Because the DBT oxidation reaction takes place inside the pores, it was important to assess the transport constraints during the reaction. DBT was oxidized at different mixing rates

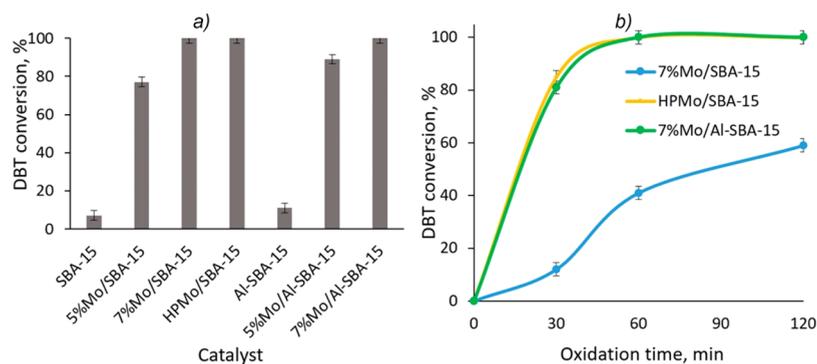


Figure 5. Effect of catalyst nature on DBT conversion. Oxidation conditions: (a) 60 °C, 30 min, 0.5% wt cat, H₂O₂/S = 6:1; (b) 60 °C, 0.25% wt cat, H₂O₂/S = 6:1.

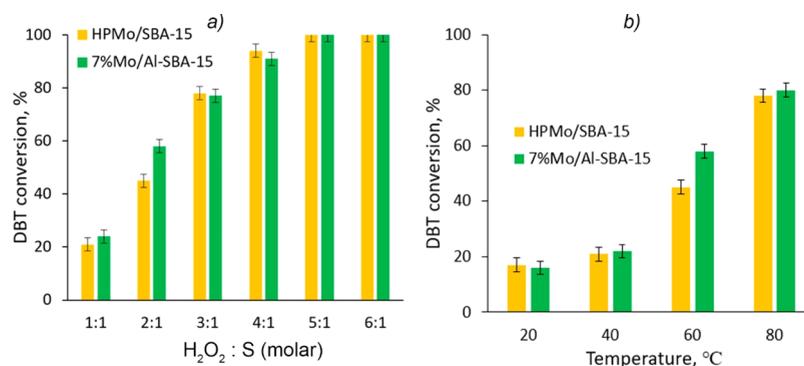


Figure 6. Effect of quantity of hydrogen peroxide (a) and temperature (b). Oxidation conditions: (a) 60 °C, 30 min, 0.5% wt cat.; (b) 30 min, 0.5% wt cat., H₂O₂/S = 2:1.

of the reaction mixture (Figure 7). According to the data obtained, the mixing speed should be 650 rpm or higher so

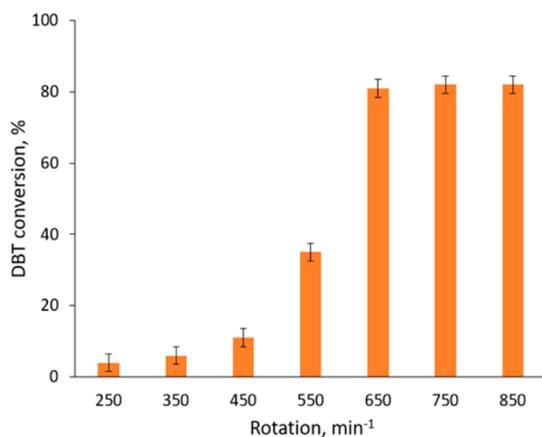


Figure 7. Effect of rotation. Oxidation conditions: 60 °C, 0.25% wt 7% Mo/Al-SBA-15, H₂O₂/S = 6:1, 30 min.

that transport restrictions can be considered insignificant.⁴⁷ With a decrease in the stirring frequency, an equable distribution of the solid catalyst in the volume of the model mixture is not achieved, which leads to a decrease in DBT conversion. In this regard, all the values given in this paper are obtained by stirring at 650 rpm.

Various classes of sulfur compounds were also oxidized (Figure 8). Oxidation was performed under conditions in which complete DBT conversion was achieved: 60 °C, 30 min, 0.5% wt catalyst, H₂O₂/S = 6:1. The initial content of total

sulfur in all model mixtures was 500 ppm. The following sulfur-containing compounds were oxidized: methyl phenyl sulfide (MeSPh), dibenzyl sulfide (Bn₂S), benzothiophene (BT), 5-methylbenzothiophene (MeBT), 4-methylDBT (MeDBT), and 4,6-dimethylDBT (Me₂DBT).

The methyl group in the structure of benzo- and DBT negatively affects the conversion of DBT for 7% Mo/Al-SBA-15. At the same time, the presence of two methyl groups in DBT almost negates this effect. The addition of methyl groups leads to an increase of electron density on the sulfur atom from one hand. On the other hand, addition of methyl groups creates steric hindrances for sulfur atoms. From literature data, it is known that electron density on the sulfur atom for dimethylDBT is slightly higher than methylDBT,⁴⁸ which probably can be the reason for the obtained results. However, for the catalyst HPMo/SBA-15, it can be seen that the oxidation of branched derivatives is difficult, which is due to the smaller pore size of the catalyst and the resulting steric difficulties, which was shown above by comparison of catalyst textural properties. Significantly lower BT conversion in oxidation reactions is associated with a lower electron density on the sulfur atom.⁷

The proposed cycle of oxidation is shown in Figure 9. According to the suggested mechanism, the presence of aluminum in the support leads to the formation of Brønsted acid sites, which coordinates sulfur-containing compounds in the catalyst's pores. This probably explains why phosphomolybdic acid over nonacidic SBA-15 shows the same results as MoO₃ over acidic Al-SBA-15. Molybdenum oxide is connected with the surface of the support with a hydrogen bond, which

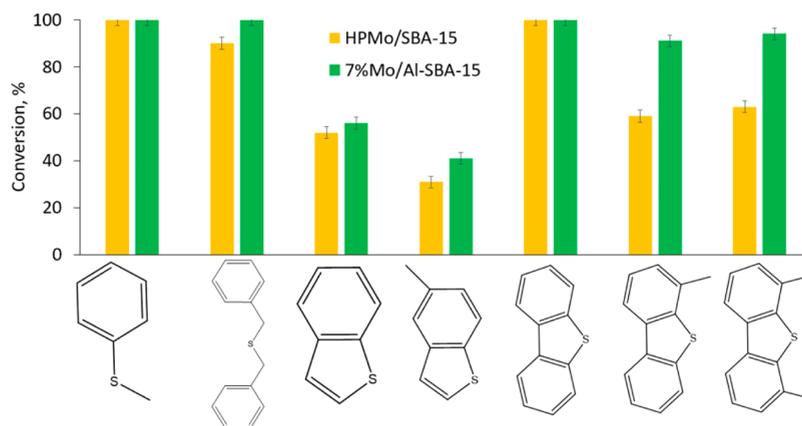


Figure 8. Oxidation of different sulfur-containing compounds. Oxidation conditions: (a) 60 °C, 30 min, 0.5% wt cat, $H_2O_2/S = 6:1$.

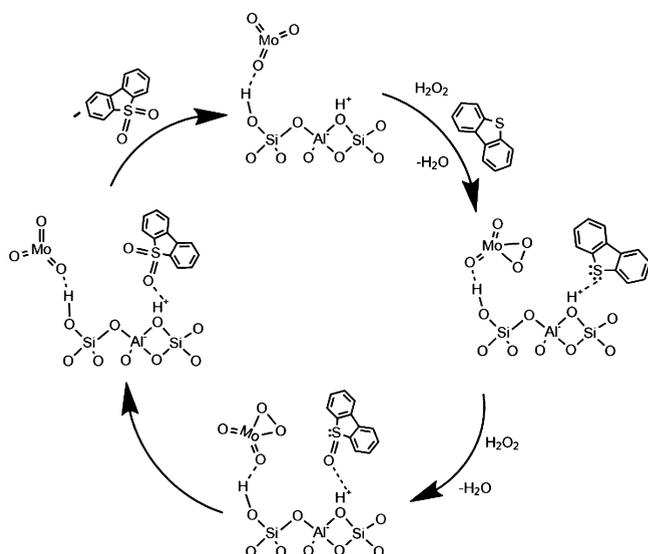


Figure 9. Proposed cycle of oxidation.

allows prevention of leaching of active sites and is proved by elemental analysis of the regenerated catalyst.

Because synthesized catalysts are planned to be used for oxidative desulfurization of real fuels, it is important to estimate the maximum concentration of sulfur compounds that can be removed in the presence of both catalysts. For this purpose, a model mixture of DBT with a sulfur content from

250 to 2000 ppm was obtained. Figure 10a shows that when the initial sulfur content increases from 500 to 1000 ppm, the DBT conversion rate decreases sharply. This effect can be explained by filling the pores of the catalyst with oxidation products (DBT sulfone), which is easily adsorbed in the pores because of their high polarity. In this regard, after each oxidation cycle, it is necessary to regenerate the catalyst. It is important to note that the pore filling of the catalyst HPMo/SBA-15 is faster than that of the catalyst 7% Mo/Al-SBA-15. This is because of the smaller size of the pores for the phosphomolybdic acid-containing catalyst.

Regeneration of the catalyst was performed by washing it with acetone and then drying it in the air current at 100 °C to completely remove water and acetone. As can be seen from Figure 10b, washing the catalyst with acetone allows maintaining the efficiency of the catalyst for at least 10 cycles. Studies of the effect of the number of regenerations on DBT conversion were performed on a model mixture containing 500 ppm of sulfur.

The composition of model mixtures before and after oxidation is shown in Figure 11. As can be seen from the chromatograms, there is no sulfoxide in the oxidation products, which indicates that the reaction is complete before the formation of sulfone. Figure 11 also shows the acetone chromatogram after catalyst regeneration. It is important to note that the peak of DBT is not observed in acetone, and, consequently, DBT is not adsorbed into the pores of the catalyst but fully reacts. The presence of a peak of DBT sulfone

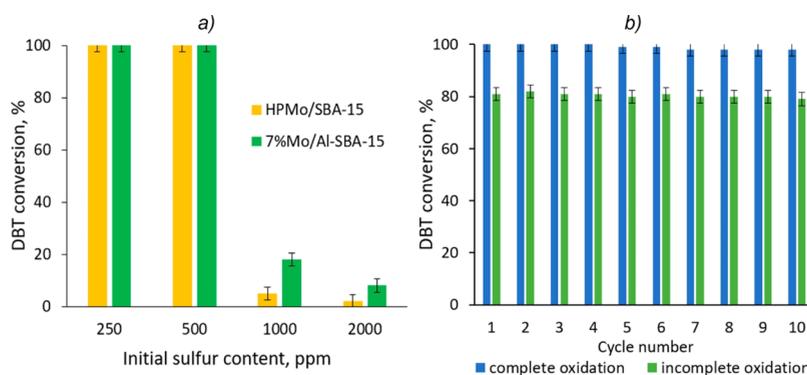


Figure 10. Effect of initial sulfur content (a) and regeneration of the catalyst (b) on DBT conversion. Oxidation conditions: (a) 60 °C, 30 min, 0.5% wt cat, $H_2O_2/S = 6:1$; (complete oxidation) 60 °C, 30 min, 0.5% wt 7% Mo/Al-SBA-15, $H_2O_2/S = 6:1$; (incomplete oxidation) 60 °C, 30 min, 0.25% wt 7% Mo/Al-SBA-15, $H_2O_2/S = 6:1$.

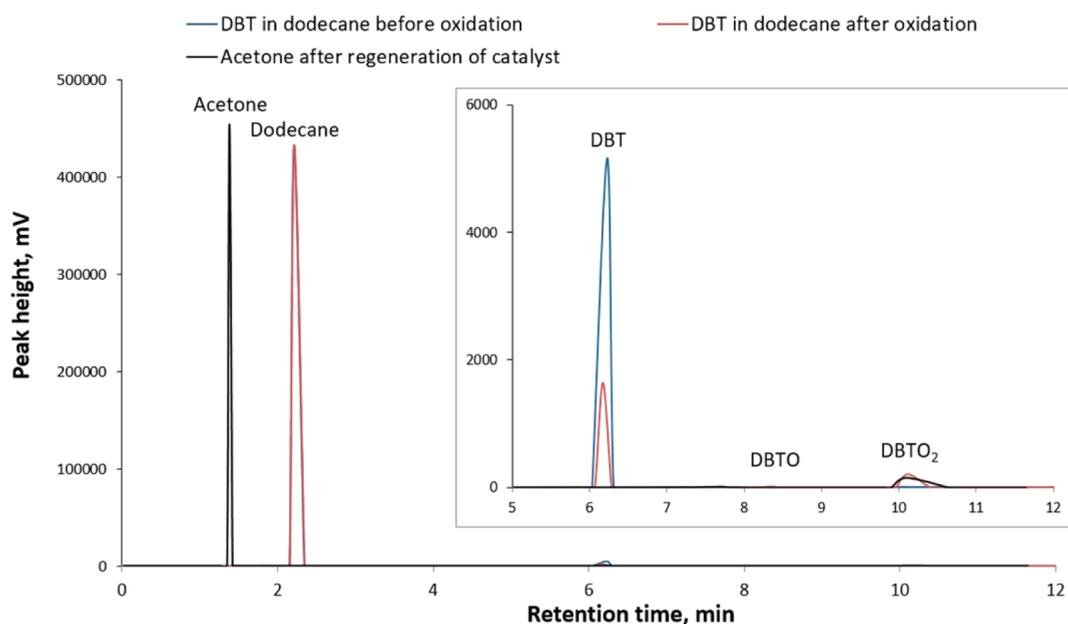


Figure 11. Chromatograms of DBT in dodecane before and after oxidation (oxidation conditions: 60 °C, 30 min, 0.5% wt 7% Mo/Al-SBA-15, $H_2O_2/S = 2:1$) and acetone after regeneration of the catalyst.

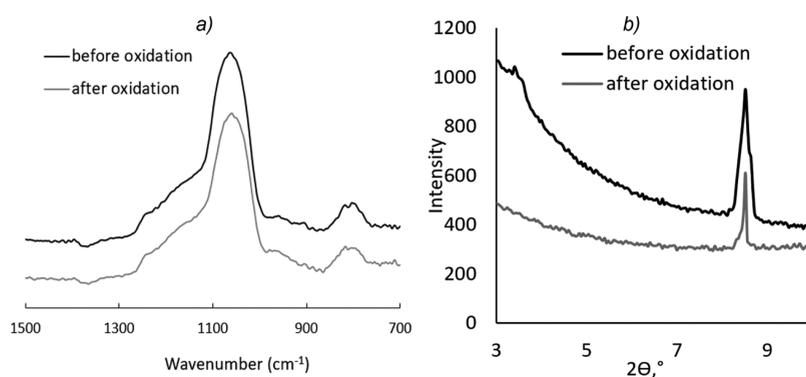


Figure 12. FTIR-spectrum (a) and XRD-spectrum of 7% Mo/Al-SBA-15 before oxidation and after oxidation and regeneration.

Table 2. Comparison of Catalytic Systems for Oxidative Desulfurization

catalyst	substrate	oxidation conditions	conversion, %	TOF ^a , 10 ⁻³	references
7% Mo/Al-SBA-15 (100)	DBT	60 °C, 30 min, 0.5% wt cat., $H_2O_2/S = 5:1$	100	2,5	this paper
HPMo-IL/SBA-15 (IL - 1-methyl-3-(trimethoxysilylpropyl)-imidazolium chloride)	DBT	60 °C, 90 min, 0.3% wt cat., $H_2O_2/S = 2:1$	90.6	1,5	49
SBA-15 + ImCl + MoO(O ₂) ₂	MeSPh	25 °C, 60 min, 3% wt cat., $H_2O_2/S = 1:1$	95		50
PMoV ₂ /SBA-15-NH ₂	DBT	60 °C, 120 min, 0.32% wt cat., $H_2O_2/S = 16:1$	97.8	0,3	51
20% MoO ₃ /SBA-15 + formic acid	4,6-Me ₂ DBT	70 °C, 30 min, 0.25% wt cat., $H_2O_2/S = 10:1$, $H_2O_2/\text{formic acid} = 1.5$	99		52

^aValues of TOF are calculated for the catalysts used in the oxidation of DBT as a substrate.

in acetone after washing the catalyst confirms the strong influence of sulfone adsorption on the catalyst's activity at low temperatures.

The physical and chemical characteristics of 7% Mo/Al-SBA-15 after oxidation were also studied. Figure 2f shows that the hexagonal structure and parallel pore arrangement are preserved after oxidation. The IR spectrum of the catalyst after oxidation is completely identical to the spectrum before oxidation (Figure 12a). The XRD spectrum shows a slight decrease in the peak responsible for the crystal structure of the support (Figure 12b). However, small destruction of the

crystal structure does not affect its activity in the DBT oxidation reaction. Textural properties and elemental analysis of the spent catalyst are discussed above (Figure 1), and this proves that after 10 cycles of oxidation–regeneration, there is minimal effect on the catalyst structure and activity.

Table 2 shows that the catalysts obtained in the work differ in their simplicity of composition and efficiency in oxidation reactions even with a small excess of the oxidant. The main advantage of the obtained catalyst is its high activity, which allows them to archive complete DBT oxidation in 30 min. A comparison of TOF for different catalysts described in the

literature shows that catalyst 7% Mo/Al-SBA-15 shows even higher activity than polyoxometalate-containing analogues.

4. CONCLUSIONS

Thus, the acidic SBA-15 type modified by molybdenum oxide proved to be an effective catalyst for oxidative desulfurization with excellent activity, even better than expensive polyoxometalate-based analogues. Research in the field of new heterogeneous acidic support-based catalysts for oxidative desulfurization is promising, thanks to their effectivity, possibility of regeneration, and cost-effectivity. These materials have broad prospects in research on the oxidation of various classes of sulfur-containing compounds and the process of oxidative desulfurization.

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Author Contributions

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

Notes

The authors declare no competing financial interest.

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