Heterogeneous catalysts based on Anderson-type polyoxometales for aerobic oxidation of sulfur-containing compounds

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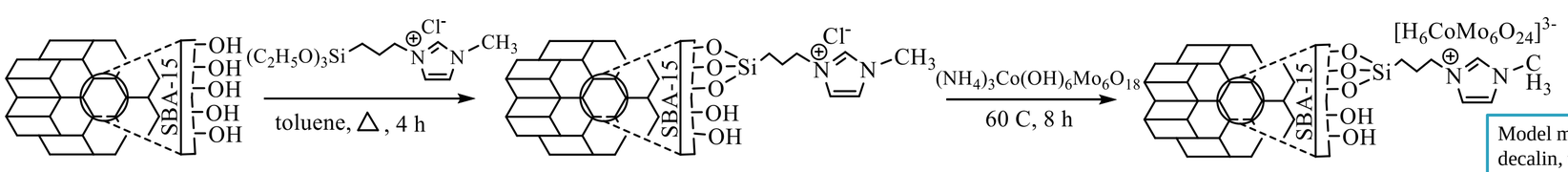
The problem of sulfur removal in oil fractions is still urgent. The annual increase in the sulfur content of produced oil has a negative impact on the environment around the world. Sulfur-containing compounds in the petroleum crude oil are toxic and corrosive substances, as well as poisons for catalysts for secondary oil processing. In many countries, the permissible values of sulfur content in commercial fuels are strictly regulated, but there is a tendency to tighten standards.

Traditional methods of desulfurization (hydrodesulfurization) include the use of expensive hydrogen-containing mixtures, the use of high pressure and temperature. Mercaptans, sulfides, and disulfides are removed during hydrodesulfurization, but hydrogenation of the main class of sulfur-containing compounds, namely condensed thiophene derivatives, is difficult due to their low reactivity. In the last decade, alternative methods for removing sulfur with a high degree of purification and based on the use of adsorbents, extractants, oxidizers, and various biologically living organisms have been proposed. The most widely known alternative method is the oxidative desulfurization (ODS), which includes the removal of sulfur-containing compounds under the action of oxidants, followed by the removal of oxidized products by extraction and adsorption methods. The use of various oxidizers is known from the literature, but the most interesting of them is air oxygen. An important advantage of using air oxygen is its availability and safety, and in the case of O_2 contained in air as an oxidizer, it is also cheap.

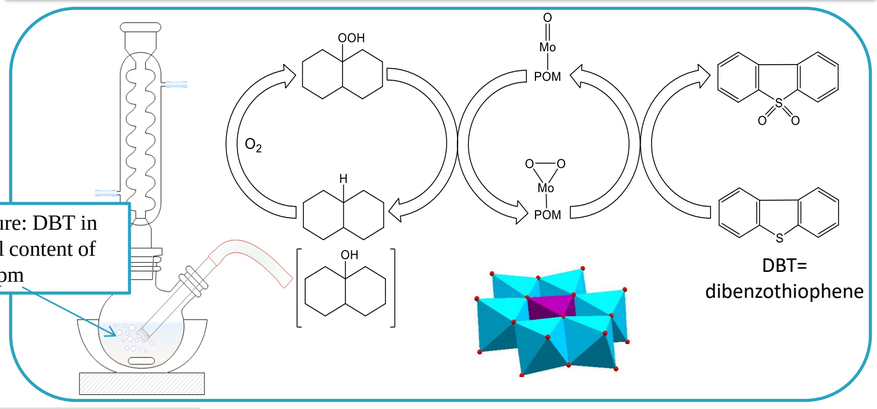
Polyoxometalates (POMs) are universal oxidation catalysts that have received wide interest as a result of high activity in the presence of oxygen or air. The advantage of polyoxometalates as aerobic oxidation catalysts over other systems is their multifunctional active center, containing protons, atoms of oxygen, and metals. Anderson-type polyoxometalates with a mixed valence of a transition metal atom, which exhibit high catalytic activity under rather mild conditions (150°C) in oxidative desulfurization reactions with atmospheric oxygen, attract great attention. Anderson-type polyoxometalates are a planar structure containing a central metal-oxygen octahedron surrounded by six edge MO_6 octahedra (where M = W or Mo). Each skeleton of a metal atom is bonded to two terminal oxygen atoms, which provide high catalytic activity in oxidation reactions of sulfur-containing substrates.

Experimental

1.1. Synthesis of immobilized Anderson-type POM on SBA-15

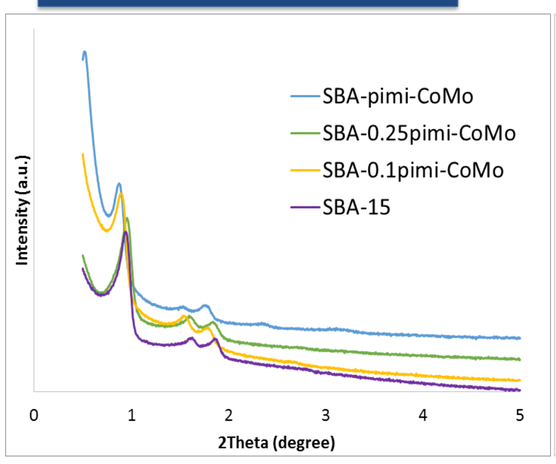


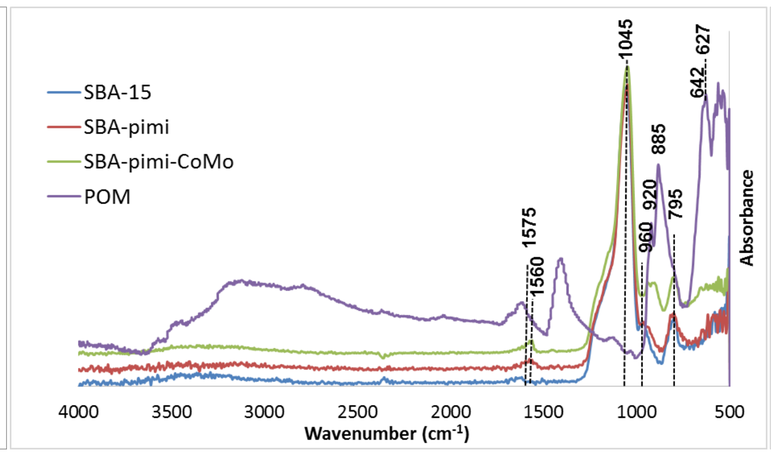
1.2. Scheme of aerobic oxidative desulfurization of feed model mixture

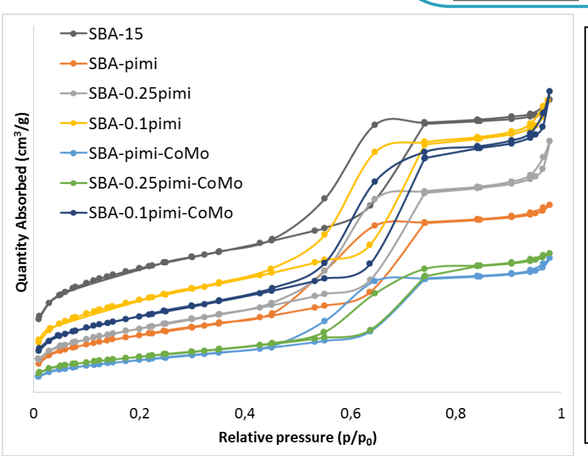


Results and discussion

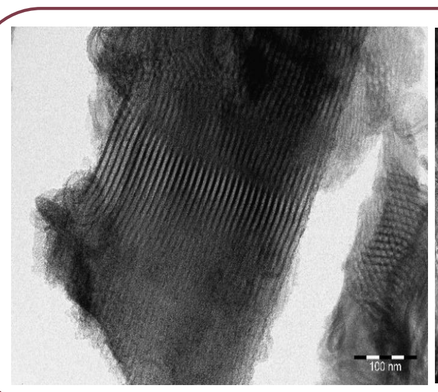
2.1. Catalyst characterization







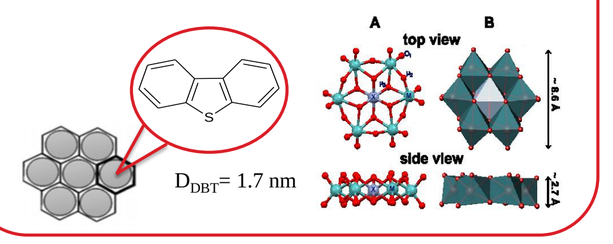
Sample	S_{BET} (m^2/g)	V_P (cm^3/g)	D_P (nm)
SBA-15	710	0.80	6.03
SBA-pimi	335	0.49	4.88
SBA-0.25pimi	376	0.65	5.43
SBA-0.1pimi	536	0.77	5.89
SBA-pimi-CoMo	196	0.35	5.36
SBA-0.25pimi-CoMo	208	0.36	5.47
SBA-0.1pimi-CoMo	443	0.68	5.87



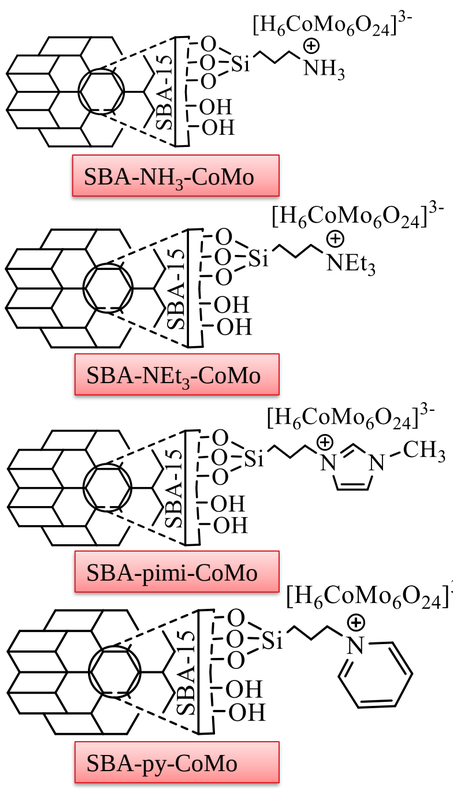
Results of elemental content by EDX

Element	keV	Mass %
C K		
N K	0.525	13.91
O K		
Si K	1.739	59.41
Cl K	2.621	0.73
Co K	6.924	2.00
Mo L	2.293	23.95

Catalysts have highly developed surface and pore diameter satisfying the requirements for diffusion of condensed thiophene derivatives

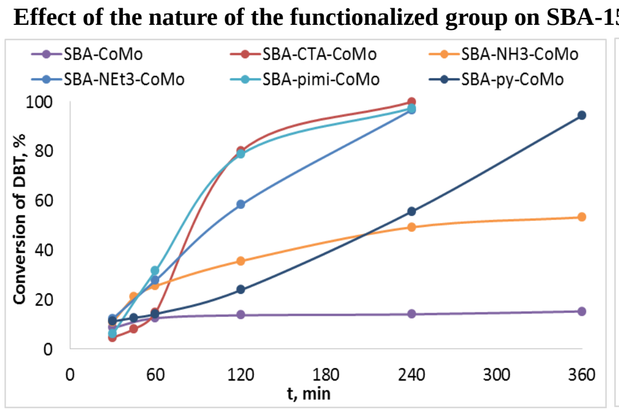


2.2. Catalytic test

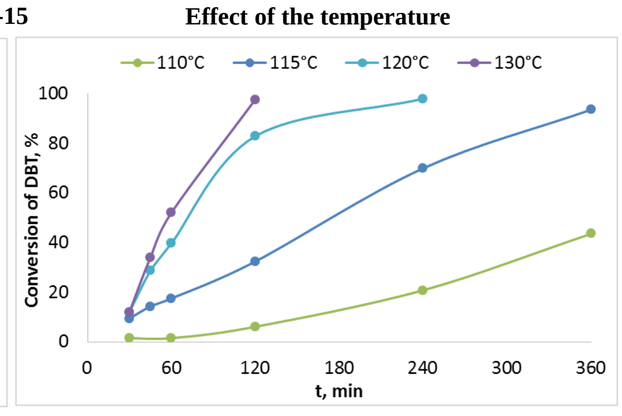


Standard condition reaction: 120°C, 0.06% catalyst, 6 l/h, 500 rpm, atmospheric pressure

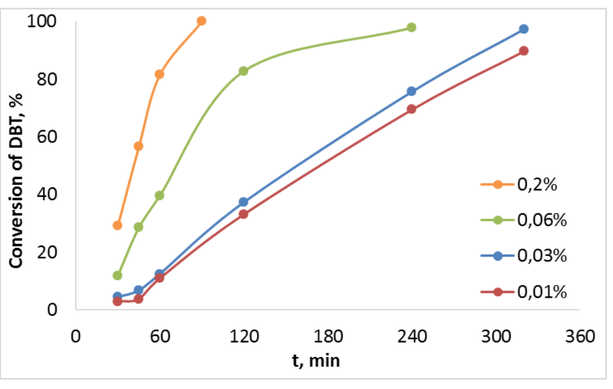
Effect of the nature of the functionalized group on SBA-15



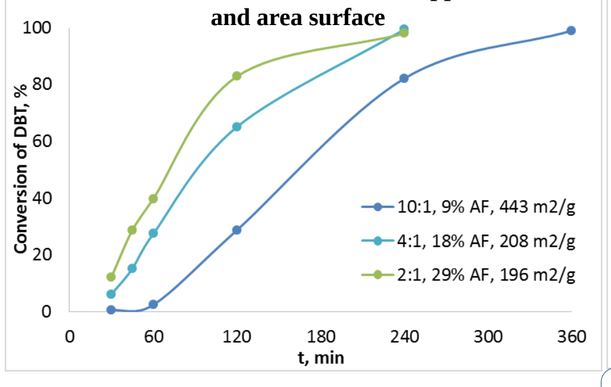
Effect of the temperature



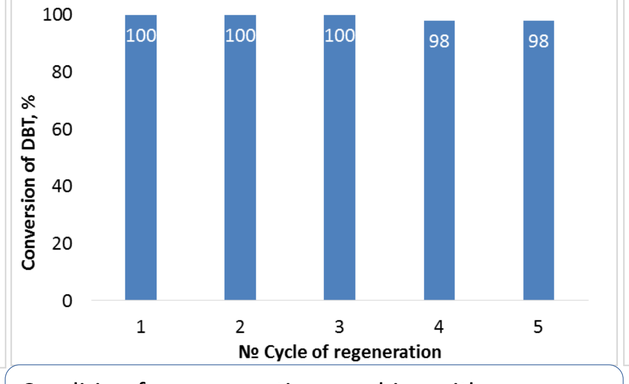
Effect of the catalyst dosage



Effect of the amount of POM on the support surface and area surface

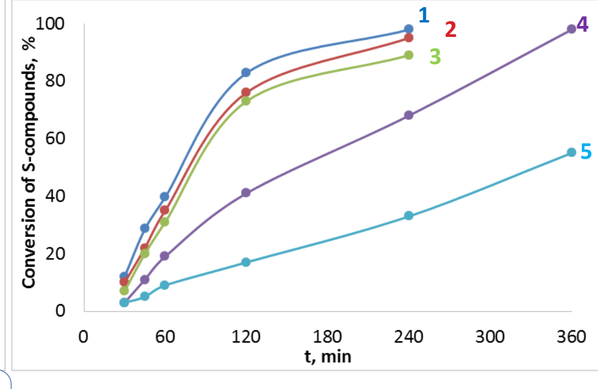


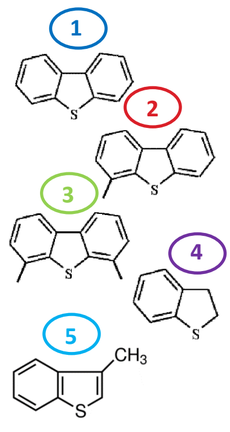
Reusability of the regenerated catalyst



Condition for regeneration: washing with excess ethanol and drying at 80-100 °C (16h)

Effect of the nature of the sulfur substrate





Conclusions

- ✓ At first time synthesized and investigated by a complex of physicochemical methods of immobilized polyoxometalate Anderson type on the surface of mesoporous silicate type SBA-15
- ✓ The optimal conditions for the oxidation of model mixture and the regularities of DBT oxidation were selected, depending on the nature of the functionalized group, the amount of polyoxometalate as an active center on the support surface and surface area of catalyst
- ✓ The effect of temperature, catalyst dosage, and nature of the sulfur substrate in the process of aerobic oxidation on the conversion of the sulfur-containing compound is shown
- ✓ The possibility of the regenerated catalyst reuse was investigated, and the conditions for regeneration of catalytic activity were determined
- ✓ Complete oxidation of dibenzothiophene was achieved in the presence of chemically grafted polyoxometalate of the Anderson type on the imidazole-functionalized SBA-15 surface at 120°C for 4 hours with an air flow of 6 l / h

Acknowledgement

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