

Synthesis and application of cobalt and polyoxomolybdate-containing alumina systems

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Abstract. The work is devoted to the synthesis and study of the activity of cobalt and polyoxomolybdate-containing alumina catalyst. The synthesized catalytic system was characterized using the following analysis methods: scanning electron microscopy, x-ray phase analysis, x-ray diffraction analysis, IR spectroscopy. It was found that the CoMo/Al₂O₃ system is active in the hydrodesulfurization reaction of model raw materials.

1. Introduction

The paramount task facing the domestic oil refining industry is its speedy modernization aimed at increasing the number of light fractions produced and bringing their quality to the necessary requirements while reducing the yield of fuel oil [1-2]. The oil refining efficiency depends on the amount of petrol and diesel, which in turn depends on the power of the secondary processes. The following heavy petroleum feedstocks can act as raw materials for oil refining processes: residues from atmospheric and vacuum distillation (fuel oil and tar, respectively), heavy vacuum gas oils, gas oils of thermal processes. The presence of primary oil distillation processes at an oil refinery allows obtaining a depth of not more than 60%. Vacuum gas oil processing achieves a depth of 70% and only the processing of heavy residues and tar allows us to obtain values of 85-90%.

The main technologies that allow the processing of heavy petroleum feedstocks of various compositions are the following processes: coking processes (batch and continuous), catalytic cracking, hydrocracking and hydro-processing (hydroconversion) using various catalytic systems and catalysts.

In recycling processes, catalysts based on transition metal compounds (cobalt and / or nickel, molybdenum and / or tungsten) are most often used as catalysts. The fundamental difference between the above catalysts (based on transition compounds) and catalysts based on platinum group metals (platinum, palladium) is the preservation of activity in the medium (heavy oil feed) with a high content of heteroatomic compounds [3].

It is known that the properties of the catalysts are largely dependent on the properties of the carrier material. As carriers for oil refining catalysts, individual oxides or mixtures thereof (aluminum, titanium, magnesium oxides, etc.), aluminosilicates, zeolites, composite and carbon materials can be used [4-9]. Despite the fact that catalytic systems based on oxides of silicon, zirconium, magnesium and titanium can be more active in secondary processes, the most widely used catalysts are based on



alumina ($\gamma\text{-Al}_2\text{O}_3$). This is due to the manifestation of the following properties of $\gamma\text{-Al}_2\text{O}_3$: low cost, thermal stability, the ability to obtain granules with the optimal size, shape and texture characteristics. The catalytic properties of oil refining catalysts are significantly affected by the composition of the active phase precursors used. Of particular interest is the use of polyoxomolybdate compounds (molybdenum blue) as active phase precursors. Previously [10], it was shown that catalytic systems obtained using molybdenum blue show activity during processing of heavy oil feedstocks. In the composition of the catalysts of recycling processes, along with Mo (W), metals promoters (Co / Ni) also appear. In this regard, the simultaneous use of Co-containing compounds and molybdenum blue for the synthesis of catalytic systems is an urgent task.

The aim of this work is the synthesis and use of alumina Co- and polyoxomolybdate-containing catalyst systems.

2. Experimental part

$\gamma\text{-Al}_2\text{O}_3$ obtained by calcining pseudoboehmite powder (Ishimbaysky Specialized Chemical Plant of Catalysts) was used as a carrier for the catalysts. Catalytic systems based on the obtained supports were prepared according to traditional methods of impregnation by moisture capacity. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (analytical grade) was used as a precursor of the Co-containing compound; molybdenum blues synthesized using the mechanical activation method and natural molybdenite were used as the precursor of the Mo-containing compound [10]. The finished catalysts were dried at 100 °C and calcined at a temperature of 550 °C. Further, the prepared catalyst systems were designated CoMo / Al_2O_3 . The physicochemical properties of the samples were studied using the following analysis methods: X-ray phase analysis (XRD), X-ray diffraction analysis (XRD), IR spectroscopy, visible spectroscopy, scanning electron microscopy. A preliminary assessment of the catalytic activity of the catalysts was carried out on a “Autoclave Engineers Bolted Closure” high pressure installation under the following conditions: temperature — 340 °C, hydrogen pressure — 30 MPa, and stirring speed — 600 rpm. As a raw material for testing the catalytic system, a model mixture was used. The initial components of the model mixture were chosen dibenzothiophene (DBT) (simulates the behavior of stable sulfur-containing compounds contained in heavy petroleum feedstocks) and normal hexadecane (acts as a solvent). The concentration of DBT in the mixture was 1000 ppm (in terms of sulfur). The activity of the catalytic system in the hydrodesulfurization reaction of the model mixture was determined by the residual sulfur content in the hydrogenates. The amount of residual sulfur in the hydrodesulfurization products was determined on a “Spectroscan S” X-ray fluorescence analyzer.

3. Discussion of the results

Figure 1 shows electron micrographs of $\gamma\text{-Al}_2\text{O}_3$ and CoMo/ Al_2O_3 obtained on its basis. The morphology of both samples is particles of a spheroidal (or close to it) shape. Thus, the shape of the carrier particles does not undergo significant changes when applying active components (Co- and Mo-containing).

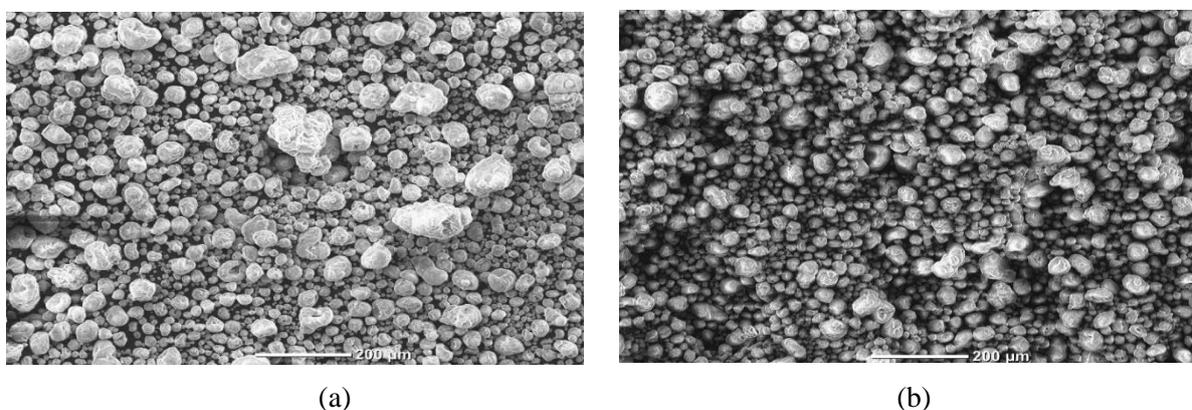


Figure 1. Electron microphotography of samples: a – aluminium oxide ($\gamma\text{-Al}_2\text{O}_3$) b – CoMo/ Al_2O_3 .

Figure 2 shows the x-ray diffraction pattern of alumina (γ - Al_2O_3). In the diffraction pattern of γ - Al_2O_3 , wide reflections are observed in the range of angles 2θ 35-40 ° and 58-64 °. In addition to the above wide reflexes, relatively well crystallized reflections characteristic of the cubic modification of γ - Al_2O_3 are fixed.

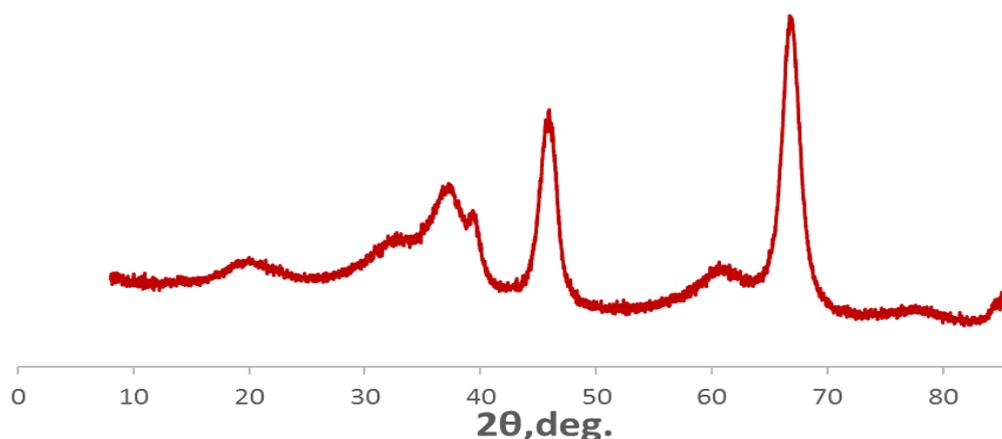


Figure 2. X-ray diffraction pattern of γ - Al_2O_3 .

The X-ray diffraction pattern (Figure 3) of the $\text{CoMo}/\text{Al}_2\text{O}_3$ catalyst system is similar to that of γ - Al_2O_3 . Reflections characteristic of Co-containing phases (CoO , Co_3O_4) and Mo-containing phases (MoO_2 , MoO_3 , MoS_2) were not detected. This is probably due to their low dispersion and low content.

Table 1 shows the X-ray structural data of the samples: the region of coherent scattering (CSR), microstresses ($\Delta d/d$), unit cell parameters (a , c). Analysis of structural data was carried out using the Rietveld structure thinning method. The calculation results show an increase in CSR from γ - Al_2O_3 to $\text{CoMo}/\text{Al}_2\text{O}_3$ (from 4.16 to 10.64 nm, respectively). This is probably due to the processes associated with the preparation of the catalytic system (impregnation with active components, drying and calcination). At the same time, microstresses and unit cell parameters of γ - Al_2O_3 decrease compared to similar parameters for $\text{CoMo}/\text{Al}_2\text{O}_3$ (for example, microstresses - from $8.1 \cdot 10^{-3}$ to $6.29 \cdot 10^{-3}$). It should be noted that the unit cell parameters vary very slightly.

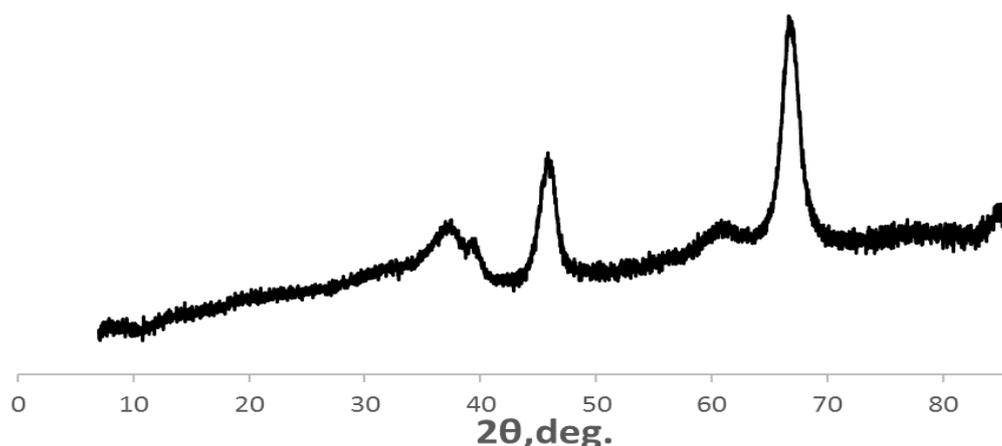


Figure 3. X-ray diffraction pattern of $\text{CoMo}/\text{Al}_2\text{O}_3$.

The IR spectra of the samples (γ - Al_2O_3 and $\text{CoMo}/\text{Al}_2\text{O}_3$) have a similar profile (Figure 4). Both samples are characterized by absorption bands in the following regions: 670 - 400 cm^{-1} , 1000 - 680 cm^{-1} ,

1400-1010 cm^{-1} , 1690-1590 cm^{-1} , 3700-2990 cm^{-1} . In this case, the main difference in the IR spectra lies in the more intense wide absorption bands in the region of 1000-400 cm^{-1} .

Table 1. X-ray results

Sample	CSR [nm]	$\Delta d/d \cdot 10^{-3}$	Parameters of unit space [\AA]	
			a	c
$\gamma\text{-Al}_2\text{O}_3$	4.16	8.1	5.6484	7.8693
CoMo/ Al_2O_3	10.64	6.29	5.6470	7.7952

It is likely that this may be due to the overlap of the absorption band related to the tetrahedral data, consists of $\gamma\text{-Al}_2\text{O}_3$, which can be due to stretching and deformation vibrations of Mo-O and Mo-O-Mo, grouped in the components of the catalytic system.

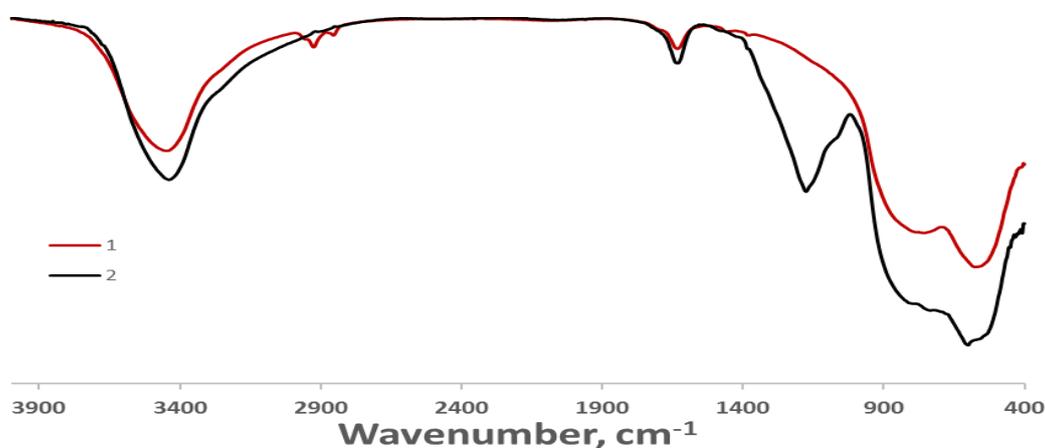


Figure 4. The IR spectra of the samples
1 - $\gamma\text{-Al}_2\text{O}_3$, 2 - CoMo/ Al_2O_3 .

Testing of the catalytic system (CoMo/ Al_2O_3) in the hydrodesulfurization reaction of the model mixture showed its activity. As can be seen from figure 5, in the presence of CoMo/ Al_2O_3 , it was possible to reduce the residual sulfur content in the hydrogenate to a level of ~ 150 ppm (DBT conversion was about 85%). It should be noted that in the presence of $\gamma\text{-Al}_2\text{O}_3$, a decrease in the sulfur content in the reaction products was practically not observed.

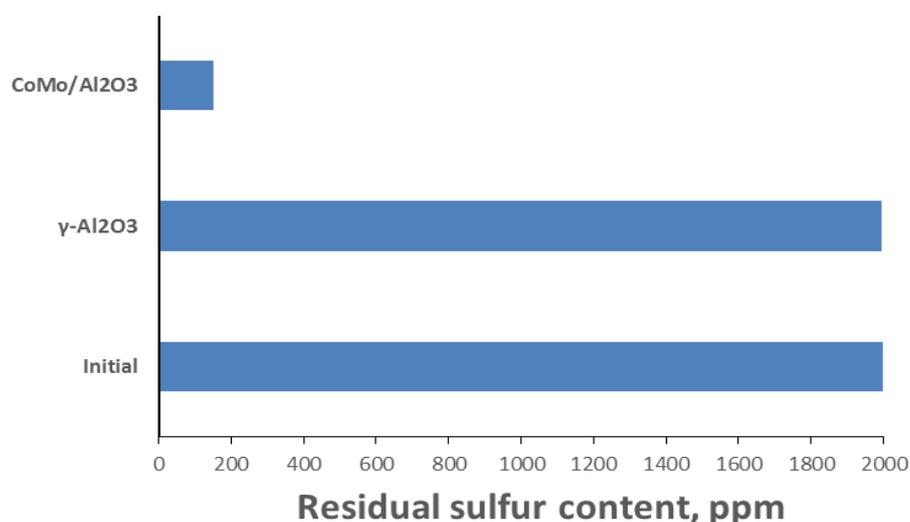


Figure 5. Residual content in hydrogenate.

4. Conclusion

As a result of the studies, a number of alumina Co- and polyoxomolybdate-containing catalysts were synthesized. A distinctive feature of the synthesis from similar studies is the following point - the use of a molybdenum blue solution as a Mo-containing precursor. The synthesized catalysts were tested in the hydrodesulfurization of model raw materials. The DBT conversion was ~ 85%, and the sulfur content in the reaction products decreased to 153 ppm.

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