The influence of phosphorus and Mo loading on the MoS\(_2\) phase morphology and performance of sulfided Mo/Al\(_2\)O\(_3\) catalysts in HDO of rapeseed oil

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Abstract: - The effect of Mo loading on the dispersion of sulfide phase and catalytic activity of MoS\(_2\)/Al\(_2\)O\(_3\) catalysts in the rapeseed HDO was studied. Five catalysts with Mo loading between 10 and 16 wt.% were prepared by impregnation of alumina with aqueous solutions containing MoO\(_3\), H\(_3\)PO\(_4\) and citric acid, subsequent drying and high-pressure sulfidation. HDO activity of the MoS\(_2\)/Al\(_2\)O\(_3\) catalysts was enhanced with the Mo content increase from 10 to 12 wt.% and then was decreased with the further increase of Mo loading. The behavior of MoS\(_2\)/Al\(_2\)O\(_3\) and P-MoS\(_2\)/Al\(_2\)O\(_3\) catalysts with the same Mo loading (near 14 wt.%) was compared in the hydrodeoxygenation of rapeseed oil demonstrating the higher activity of P-promoted system. The modeling of XRD patterns with using of the Debye Function Analysis (DFA) gives the lower d\(_{\text{XRD}}\) of the MoS\(_2\) particles in the P-MoS\(_2\)/Al\(_2\)O\(_3\) catalyst in comparison with MoS\(_2\)/Al\(_2\)O\(_3\) one. We proposed that P incorporation in the MoS\(_2\) slabs can result in a higher deformation of the supported MoS\(_2\) particles, which in turn could have been a reason of higher activity of P-MoS\(_2\)/Al\(_2\)O\(_3\) catalyst.

Key-Words: - hydrotreatment, hydrodeoxygenation, MoS\(_2\), sulfide catalyst, rapeseed oil, co-processing

1 Introduction

The development of new catalytic processes for the production of liquid motor fuels from the renewables is stimulated by the growing demand for transportation fuels along with the decrease in oil reserves and vital tendency to reduce the greenhouse gas emissions. The hydrotreatment of triglyceride-based feedstock, namely vegetable oils, waste cooking oil, animal fats, etc., produces the mixture of C\(_{12}:C_{18}\) alkanes, which are the valuable components of the petroleum-based motor fuels [1]. The conventional hydrotreating catalysts (CoMo/Al\(_2\)O\(_3\) or NiMo/Al\(_2\)O\(_3\)) are widely used for the hydrodeoxygenation (HDO) of triglyceride-based feedstocks [2-5] or their mixture with petroleum-derived fractions [5-11].

2 Problem Formulation

The HDO of triglycerides over sulfide Co(Ni)Mo/Al\(_2\)O\(_3\) catalysts proceeds through the so-called direct deoxygenation route producing water or via decarbonylation pathway, giving CO among the final products along with alkanes [12,13]. The production of CO and CO\(_2\) in the HDO processes is highly undesirable because of several ecological and technological reasons [4,5]. The conversion of triglycerides via decarbonylation reaction led to decrease in the yield of the liquid products and could cause the formation of CH\(_4\) and CO\(_2\) via the hydrogenation or the water gas shift reaction. CO\(_2\) in the presence of water can form carbonic acid and causes corrosion of the equipment. The accumulation of CH\(_4\) and CO in the recycle gas would decrease the partial pressure of hydrogen, which is the critical parameter for the production of sulfur-free motor fuels from the mixture of petroleum oil with triglyceride-based feedstock [14]. The activity of a CoMo/Al\(_2\)O\(_3\) catalyst in hydrodesulfurization reactions of diesel fractions decreases in the presence of triglyceride feedstock [15–17], presumably, as a result of inhibition of HDS and HDN reactions with carbon monoxide [17,18]. The non-promoted sulfide Mo/Al\(_2\)O\(_3\) catalysts were shown to provide RSO conversion without considerable CO\(_x\) formation [19-21], that makes them the promising candidates for the HDO of triglycerides. Recently, the dual-bed catalytic system consisting of MoS\(_2\)/Al\(_2\)O\(_3\) and Co–MoS\(_2\)/Al\(_2\)O\(_3\) catalysts is proposed for the production of ULSD from a straight-run gas oil mixed with rapeseed oil (10–45 wt %).
conversion of rapeseed oil to alkanes proceeds in the bed of MoS2/Al2O3 catalyst via the route of “direct” hydrodeoxygenation without the formation of carbon oxides, while the HDS of gas oil occurs in the bed of the Co–MoS2/Al2O3 hydrotreating catalyst [22]. So, the use of MoS2/Al2O3 catalyst for the HDO of triglycerides or for the HDT of triglycerides/SRGO mixture aids avoiding a technological problems, increasing the yield of diesel fuel, preventing greenhouse gases formation (CH4, CO, CO2).

The effect preparation conditions on the morphology of MoS2 slabs and the HDS performance of MoS2/Al2O3 catalyst were thoroughly investigated [23-26], while there are no similar investigations concerning HDO reactions. In our work the effect of Mo loading and phosphor on the performance of MoS2/Al2O3 catalysts in HDO of rapeseed oil was investigated. Catalysts were prepared by an impregnation method with or without addition of phosphoric acid in the impregnation solution, prepared from MoO3 and citric acid.

3 Problem Solution

3.1 Experimental

Mo/Al2O3 catalysts were prepared by impregnation of alumina granules (BET surface area 208 m² g⁻¹, pore volume 0.68 ml g⁻¹, average pore diameter 13.2 nm, purchased by JSK “Promkataliz”, Ryazan, Russia) with aqua solutions containing citric acid, H3PO4 and different amount of MoO3, (all purchased by Vekton, Russia). The catalyst designation and chemical composition are given in Table 1. To investigate the influence of phosphorus addition sample “HDO-6” was prepared without the addition of phosphoric acid to impregnation solution. The catalysts were dried in nitrogen flow at room temperature and then at 110°C for 4 h.

Table 1. The chemical composition of the catalysts

<table>
<thead>
<tr>
<th>Designation</th>
<th>Mo, wt%</th>
<th>P, wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDO-1</td>
<td>10.1</td>
<td>1.6</td>
</tr>
<tr>
<td>HDO-2</td>
<td>11.0</td>
<td>1.5</td>
</tr>
<tr>
<td>HDO-3</td>
<td>12.4</td>
<td>1.7</td>
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<tr>
<td>HDO-4</td>
<td>13.9</td>
<td>1.6</td>
</tr>
<tr>
<td>HDO-5</td>
<td>16.0</td>
<td>2.3</td>
</tr>
<tr>
<td>HDO-6</td>
<td>13.8</td>
<td>0</td>
</tr>
</tbody>
</table>

The textural properties of the catalysts were determined using nitrogen physisorption with an ASAP 2400 instrument (USA); the elemental analysis was performed using Optima 4300 D V (Perkin Elmer, France). The morphology of sulfide phase was studied using a JEO-L electron microscope (JEOL, Japan) with 1.4 Å lattice resolution at a 200 kV accelerating potential. Prior to the study, the samples were ground, suspended in ethanol and placed on a copper grid coated with a holey carbon film. XRD investigations were carried out at an ARL X'TRA diffractometer (Thermo, Switzerland) with a Si(Li) solid-state detector and Cu Kα radiation. The measurements were carried out in the 20 range of 10°-80° with a step of 0.1°. Phase analysis was performed using the ICDD PDF-2 database.

The catalytic experiments were performed in a trickle-bed down-flow reactor with an inner diameter of 16 mm and length of 570 mm. In each experiment 10 ml of catalyst (full-sized granules) was diluted by an inert material, carborundum (0.1–0.25 mm size fraction) in a 1:2 volume ratio [27]. The catalysts were examined after sulfidation with straight-run gas oil containing additionally 0.6 wt. % sulfur as dimethyl disulfide (at H2 pressure 3.5 MPa; H/C – 300 Nm³/m³; LHHSV – 2 hour⁻¹). The sulfidation was performed at 340°C during 6 h (heating rate was 25°C in hour). The catalytic experiments were performed at H2 pressure 4.0 MPa, H/C – 600 Nm³/m³; LHHSV – 1.5 h⁻¹, temperature – 260, 280, 300, 320 and 340°C; using mixture of 20 wt.% of rapeseed oil (RSO) diluted with straight run gas oil (SRGO). Properties of mixture were d = 0.86 g/cm³, 2.34 wt. % O, 0.82 wt% S, 141 ppm N. The duration of each stages differing in temperature was 12 h; the residual sulfur and oxygen contents were obtained by averaging the data for three samples taken through 10, 11 and 12 h after the beginning of the current stage.

The sulfur content of the feedstock and that of the hydrogenated products were measured on a Lab-X 3500SCI energy dispersive X-ray fluorescence analyzer (Oxford Instruments, United Kingdom). The total oxygen content of the reaction mixture before and after reaction was determined using a Vario EL Cube CHNSO analyzer (Elementar Analysensysteme GmbH, Germany).

The contents of C16 and C17 alkane (the products of RSO hydrodeoxygenation) in the products were evaluated using two-dimensional gas chromatography (Agilent 7890A GC equipped with a flame-ionization detector and an Agilent flow modulator). In the first dimension, separation was fulfilled using helium as carrier gas and ZB-WAX capillary column of 25 m long with a diameter of 0.25 mm and the film thickness of 0.25 μm (Phenomenex, United States). An HP-5 column of 5 m long and 0.25 m in diameter with a film
thickness of 0.25 μm (Agilent, United States) was used for the separation of components in the second dimension. The carrier gas was hydrogen. The conditions of analysis were 70°C for 0.5 m in, 8°C/min, and 260°C for 25 min. The flow through the first column was 0.5 mL/min (helium), while the flow through the second column was 31 mL/min (hydrogen). The period of modulation was 2.2 s. The volume of the introduced sample was 0.5 μL, and the split ratio was 1:200. The chromatographic data were processed with the ChemStation (Agilent) and Image GC (Zoex) software.

Gas phase was analyzed on-line using a gas chromatograph «Chromos 1000» (Dzerzhinsk, Russia), equipped with the FID detector. The concentrations of CO and CO2 were determined in the form of methane after separation on column packed with 80/100 mesh HayeSep® («Sigma-Aldrich», St. Louis, MO, USA) and subsequent hydrogenation over reduced Pd catalyst at 340 °C.

3.2 Results and discussion

3.2.1 Characterization of the catalysts

Crystalline phases of the molybdenum sulfide catalysts were studied by Powder X-ray diffraction (XRD) analysis and high-resolution transmission electron microscopy (HRTEM).

HRTEM images of samples HDO-1, HDO-3 and HDO-5 taken after reaction demonstrate the typical surface fragments of the sulfided MoS2 particles (Fig.1). The HDO-1 catalyst with the lowest Mo content (10.1 wt.% of Mo) is characterized by the lowest values of average slab length (3.1 nm) and the stacking number (1.2), which are increased with the Mo loading increasing (table 2). For the catalyst HDO-5 with the loading of 16 wt.% of Mo slab length is increased to 4.2 nm, the stacking number is increased to 1.5.

Fig. 2 shows XRD patterns of the γ-Al2O3 support and MoS2/γ-Al2O3 catalysts taken after reaction. Highly broadened peaks in the 20 ranges of 33-35° and 58-60° were detected in the XRD patterns of the catalysts, which indicate formation of highly dispersed MoS2 phase.

The formation of the poorly crystallized MoS2 phase was revealed in the catalysts (JCPDS#37-1492, a=b=3.161 Å, c=12.299 Å, α=β=90°, γ=120°). Disappearance of the first (002) reflection indicates the small size of coherently scattering domain (dXRD) in the [001] direction, in which the skeletal MoS2 layers are packed.

The data obtained from HRTEM and XRD confirmed the formation of low crystalline highly dispersed MoS2 phase.

Table 2. HRTEM parameters of the sulfided catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Average slab length (nm)</th>
<th>Stacking number</th>
</tr>
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<tbody>
<tr>
<td>HDO-1</td>
<td>3.1</td>
<td>1.2</td>
</tr>
<tr>
<td>HDO-3</td>
<td>3.9</td>
<td>1.6</td>
</tr>
<tr>
<td>HDO-5</td>
<td>4.8</td>
<td>1.5</td>
</tr>
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</table>

Fig.1. HRTEM images of the catalysts HDO-1 (10.1 wt.% Mo), HDO-3 (12.4 wt.% Mo), HDO-5 (16.0 wt.% Mo).
3.2.2 Influence of Mo loading on HDO activity

Experiments were performed at the temperature range 260-340°C, H₂ pressure 4.0 MPa, H/C – 600 Nm³/m³; LHSV – 1.5 h⁻¹. The feed was 20 wt.% of RSO in SRGO. Complete oxygen conversion was observed at temperatures 340 and 320°C (fig.3). The lowering temperature resulted in a decrease of oxygen conversion over all catalysts (Fig.3). HDO activity of the MoS₂/Al₂O₃ catalysts was enhanced with the Mo content increase from 10 to 12.4 wt.%, HDO-3 catalyst being the most active catalyst in HDO of RSO mixed with SRGO (Fig.4). Further increase of Mo loading led to decrease of HDO activity.

It is known that non-promoted catalyst MoS₂/Al₂O₃ is less active in HDS and HDN reactions of SRGO than sulfide Co(Ni)Mo/Al₂O₃ catalysts. Temperature range of 320-340°C is enough to observe the change in HDS and HDN activities of the catalysts depending on Mo loading (Fig.5). The HDO-3 catalyst, as in the case of HDO, is the most active in HDS and HDN reactions of SRGO in presence of rapeseed oil. Such dependencies of catalytic activity on Mo loading can be explained by the change of active sites quantities along with the increase of particle sizes. At first, the overall quantities of MoS₂ edge sites, which are the active sites for the HDS and HDO reactions, are increased with Mo loading to some value. But with the increase of slab sizes caused by increase of Mo loading the quantities of MoS₂ edge sites go through the maxima and start to decrease at some value.
phase analysis and the results of C\textsubscript{18} and C\textsubscript{17} content measurement by means of two-dimensional chromatography. The typical chromatograms of SRGO and reaction products, obtained during HDO of RSO/SRGO mixture over MoS\textsubscript{2} at 340°C is presented in Fig.6. The quantitative analysis of C\textsubscript{18} and C\textsubscript{17} in the reaction products and in the SRGO let us to calculate the selectivity of octadecane formation that lies within the region 97-99\% for both catalysts at whole conversion of RSO (at 320 and 340°C).

The results of CO\textsubscript{x} analysis in the exit gas flow confirmed the high selectivity of RSO hydrodeoxygenation though the “direct” HDO route over all catalysts. CO\textsubscript{x} content was negligible at 260°C (about 0.04 vol.\%) and slightly increased (up to 0.10-0.12 vol.\%), with the temperature raising from 260 to 340°C. But the selectivity of DeCO\textsubscript{x} pathway calculated from the gas phase analysis did not exceed 3.0\% even at 340°C.

### 3.2.3 Effect of phosphorus addition

It’s known that the small crystallite size of MoS\textsubscript{2} in hydrotreating catalysts limits application of traditional XRD methods for structure diagnostics. The Debye Function Analysis (DFA) was used to get information about the structure of MoS\textsubscript{2} nanoparticles from the XRD data. The Debye Scattering Equation (DSE) allows calculating XRD pattern of model nanoparticle with taking into account the particle shape, size, chemical composition, and atomic structure [28-31]. Calculating and fitting XRD patterns were performed using the DIANNA software [32]. To evaluate an agreement between the calculated and experimental XRD profiles, a profile discrepancy factor (R\textsubscript{p}) was determined.

Fig.7 shows the X-ray diffraction patterns of the γ-Al\textsubscript{2}O\textsubscript{3} support and MoS\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3} catalysts. The XRD patterns of the catalysts exhibit the highly broadened peaks in the 2θ ranges of 33-35° and 58-60°, which indicate formation of highly dispersed MoS\textsubscript{2} phase. Overlapping of the diffraction lines corresponding to the MoS\textsubscript{2} and γ-Al\textsubscript{2}O\textsubscript{3} phases complicates the analysis. So, the difference curves between the normalized XRD patterns of the catalyst and support were obtained (Fig.8). It was need to obtain information about structure of MoS\textsubscript{2} nanoparticles.

The formation of the poorly crystallized MoS\textsubscript{2} phase was revealed in the catalysts (JCPDS#37-1492, a=b=3.161 Å, c=12.299 Å, α=β=90°, γ=120°). Disappearance of the first (002) reflection indicates the small size of coherently scattering domain (d\textsubscript{XRD}) in the [001] direction, in which the skeletal MoS\textsubscript{2} layers are packed. HRTEM data also gave evidence of poor crystallization of the MoS\textsubscript{2} particles along the [001] direction (Fig.9). The average stacking number of 1.6 was determined in the both P-MoS\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} and MoS\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} catalysts (Table 3).

A direct modeling of XRD patterns with using the DSE was performed to determine the average size of coherently scattering domain. Starting from one MoS\textsubscript{2} unit cell, a set of model plate-like crystallites was generated by varying lengths of the crystallite edges. The simulation of XRD data confirmed the absence of significant MoS\textsubscript{2} stacking in the P-MoS\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} and MoS\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} catalysts.

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**Fig.6.** 2D-chromatograms of straight run gas oil (1) and the product obtained (2) in presence of P-MoS\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} at 340°C
Table 3. Dispersion characteristics of MoS$_2$ particles in the sulfide catalysts from the XRD and HRTEM data

<table>
<thead>
<tr>
<th></th>
<th>P-MoS$_2$/Al$_2$O$_3$</th>
<th>MoS$_2$/Al$_2$O$_3$</th>
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<tbody>
<tr>
<td></td>
<td>average slab length of MoS$_2$ crystallites according to the XRD data modeling</td>
<td></td>
</tr>
<tr>
<td>d$_{XRD}$ (nm)</td>
<td>R$_p$ (%)</td>
<td>d$_{XRD}$ (nm)</td>
</tr>
<tr>
<td>2.2x2.2</td>
<td>8.3</td>
<td>2.5x2.5</td>
</tr>
<tr>
<td>2.5x2.5</td>
<td>7.7</td>
<td>2.8x2.8</td>
</tr>
<tr>
<td>2.8x2.8</td>
<td>8.2</td>
<td>3.2x3.2</td>
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<td></td>
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<td>3.5x3.5</td>
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<tr>
<td></td>
<td></td>
<td>3.8x3.8</td>
</tr>
<tr>
<td>average slab length of MoS$_2$ particles according to the HRTEM data</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.6</td>
<td>4.9</td>
<td></td>
</tr>
<tr>
<td>average stacking number according to the HRTEM data</td>
<td>1.6</td>
<td>1.6</td>
</tr>
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</table>

Fig.10 shows the experimental difference XRD curve of the P-MoS$_2$/Al$_2$O$_3$ catalyst in comparison with calculated XRD patterns for the plate-like MoS$_2$ crystallites containing one and two MoS$_2$ layers with lateral dimensions of 2.5x2.5 nm (MoS$_2$ crystallites composed of 8x8x0.5 and 8x8x1 unit cells, respectively).

The model of one-layer thick crystallites is more appropriate for describing the experimental XRD pattern. The calculated XRD pattern for the MoS$_2$ crystallites composed of two layers differs drastically from the experimental one. The lateral dimensions of MoS$_2$ crystallites of one-layer thickness (slab length) in the P-MoS$_2$/Al$_2$O$_3$ and MoS$_2$/Al$_2$O$_3$ catalysts were refined. The sizes d$_{XRD}$ and corresponding discrepancy factors R$_p$ are listed in Table 3.
The obtained data show that MoS₂ particles in the P-MoS₂/Al₂O₃ catalyst are characterized by a lower average size of coherently scattering domain d_{XRD}. The best fitting results were obtained at the slab sizes of 2.5 and 3.2-3.5 nm for P-MoS₂/Al₂O₃ and MoS₂/Al₂O₃ catalysts, respectively. A comparison of the particle sizes evaluated from XRD and HRTEM data shows a pronounced discrepancy. The dimensions of the coherent scattering domains determined from XRD data are significantly smaller than slab length of MoS₂ determined from HRTEM data (Table 3). The discrepancy is explained by deformation of MoS₂ particles, which leads to breaking coherence. Indeed, the MoS₂ sheets observed in the HRTEM images are curved or folded (Fig. 9). A lower value of d_{XRD} in the case of P-MoS₂/Al₂O₃ catalyst seems to result from a higher degree of deformation of the supported MoS₂ particles. According to [33] the blending of MoS₂ slabs could lead to the creation of new active sites for thiophene HDS on their basal planes.

The results of catalytic tests of the MoS₂/Al₂O₃ and P-MoS₂/Al₂O₃ catalysts in the hydrotreating of RSO/SRGO mixture are presented in the Fig.11-12. Degree of RSO hydrodeoxygenation (Fig.11) was calculated using oxygen content in the raw material (mixture of RSO with SRGO) and in the liquid products measured by means of Vario EL Cube analyzer. The RSO conversion achieved 100% at 320 and 340°C over both catalysts; but P-MoS₂/Al₂O₃ catalyst demonstrated higher HDO activity at 260, 280 and 300°C (Fig.11). P-MoS₂/Al₂O₃ catalyst as well displayed higher activity in HDS of SRGO in comparison with MoS₂/Al₂O₃ catalyst in the whole temperature range (Fig.12).

Fig.11. Hydrodeoxygenation activity of P-MoS₂/Al₂O₃ and MoS₂/Al₂O₃ catalysts at different temperatures

Fig.12. Hydrodesulfurization activity of P-MoS₂/Al₂O₃ and MoS₂/Al₂O₃ catalysts at 320 and 340°C

4 Conclusion

The effect of phosphorus addition on the morphology of MoS₂ slabs and catalytic performance of sulfide Mo/Al₂O₃ catalysts in the HDO of rapeseed oil was also studied. MoS₂/Al₂O₃ catalyst was obtained by the impregnation of alumina with water solution obtained from MoO₃ and citric acid; during P-MoS₂/Al₂O₃ catalyst preparation H₃PO₄ was added to the same solution. The investigation of the sulfide MoS₂/Al₂O₃ and P-MoS₂/Al₂O₃ catalysts with XRD methods accompanied with Debye Function Analysis led us to conclusion, that sulfide particles in the P-MoS₂/Al₂O₃ catalysts are characterized by a lower average size of coherently scattering domain d_{XRD}. A lower value of d_{XRD} in the case of P-MoS₂/Al₂O₃ catalyst seems to result from a higher degree of deformation of MoS₂ slabs, which in turn could have been a reason of higher activity of P-MoS₂/Al₂O₃ catalyst in HDO and HDS reactions.

The effect of Mo loading on the dispersion of sulfide phase and catalytic activity of P-MoS₂/Al₂O₃ catalysts in the rapeseed HDO was also studied. With the increase of Mo loading the activities of P-MoS₂/Al₂O₃ catalysts in HDO, HDS and HDN reactions go through the maxima with the optimum Mo content – 12.4 wt%. The most probable reason of such dependencies is the coinciding change of the overall quantities of MoS₂ edge sites that is caused by the increase of sizes of MoS₂ slabs.

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References:


