The influence of phosphorus and Mo loading on the MoS_2 phase morphology and performance of sulfided Mo/Al_2O_3 catalysts in HDO of rapeseed oil

EVGENIYA N. VLASOVA [a,b], VERA P. PAKHARUKOVA [a], GALINA A. BUKHTIYAROVA[a,b], IRINA V. DELIY [a,b], PAVEL V. ALEKSANDROV [a,b], ALEKSANDER A. PORSIN, EVGENY YU. GERASIMOV[a,b], VALERII I. BUKHTIYAROV[a,b]
[a] – Boreskov Institute of Catalysis SB RAS, 630090, Pr. Lavrentieva 5, Novosibirsk, RUSSIA.
[b] – Novosibirsk National Research University, 630090, Pirogova Street 2, Novosibirsk, RUSSIA
evgenia@catalysis.ru

Abstract: - The effect of Mo loading on the dispersion of sulfide phase and catalytic activity of MoS_2/Al_2O_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_3PO_4 and citric acid, subsequent drying and high-pressure sulfidation. HDO activity of the MoS_2/Al_2O_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_2O_3 and P-MoS_2/Al_2O_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_{XRD} of the MoS_2 particles in the P-MoS_2/Al_2O_3 catalyst in comparison with MoS_2/Al_2O_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_2O_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 hydroprocessing 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 ($CoMo/Al_2O_3$ or $NiMo/Al_2O_3$) 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 $Co(Ni)Mo/Al_2O_3$ 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 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 $CoMo/Al_2O_3$ 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_2O_3 catalysts were shown to provide RSO conversion without considerable COx 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_2O_3 and $Co–MoS_2/Al_2O_3$ catalysts is proposed for the production of ULSD from a straight-run gas oil mixed with rapeseed oil (10–45 wt %). The

The obtained data show that MoS_2 particles in the P-MoS_2/Al_2O_3 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-MoS_2/Al_2O_3 and MoS_2/Al_2O_3 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 MoS_2 determined from HRTEM data (Table 3). The discrepancy is explained by deformation of MoS_2 particles, which leads to breaking coherence. Indeed, the MoS_2 sheets observed in the HRTEM images are curved or folded (Fig. 9). A lower value of d_{XRD} in the case of P-MoS_2/Al_2O_3 catalyst seems to result from a higher degree of deformation of the supported MoS_2 particles. According to [33] the blending of MoS_2 slabs could led to the creation of new active sites for thiophene HDS on their basal planes.

The results of catalytic tests of the MoS_2/Al_2O_3 and P-MoS_2/Al_2O_3 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-MoS_2/Al_2O_3 catalyst demonstrated higher HDO activity at 260, 280 a nd 300°C (Fig.11). P-MoS_2/Al_2O_3 catalyst as well displayed higher activity in HDS of SRGO in comparison with MoS_2/Al_2O_3 catalyst in the whole temperature range (Fig.12).

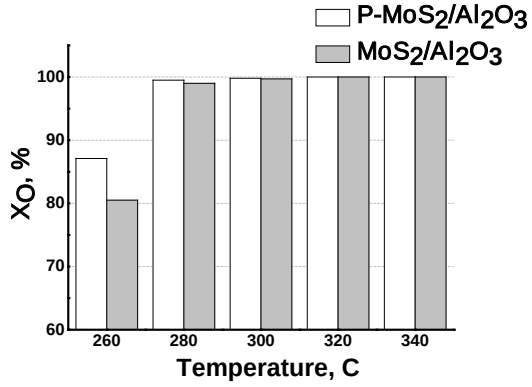

Fig.11. Hydrodeoxygenation activity of P-MoS_2/Al_2O_3 and MoS_2/Al_2O_3 catalysts at different temperatures

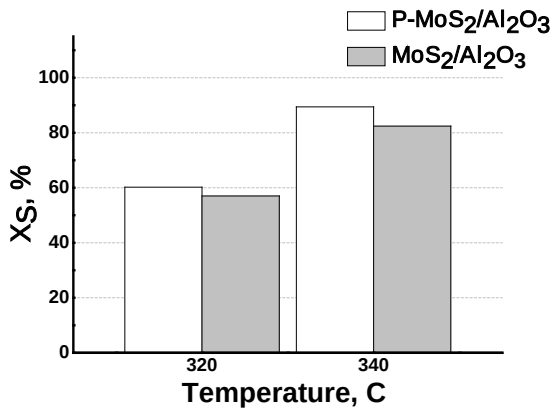

Fig.12. Hydrodesulfurization activity of P-MoS_2/Al_2O_3 and MoS_2/Al_2O_3 catalysts at 320 and 340°C

4 Conclusion

The effect of phosphorus addition on t he morphology of MoS_2 slabs and catalytic performance of sulfide Mo/Al_2O_3 catalysts in the HDO of rapeseed oil was also studied. MoS_2/Al_2O_3 catalyst was obtained by the impregnation of alumina with water solution obtained from MoO_3 and citric acid; during P-MoS_2/Al_2O_3 catalyst preparation H_3PO_4 was added to the same solution. The investigation of the sulfide MoS_2/Al_2O_3 and P-MoS_2/Al_2O_3 catalysts with XRD methods accompanied with Debye Function Analysis led us to conclusion, that sulfide particles in the P-MoS_2/Al_2O_3 catalysts are characterized by a l ower average size of coherently scattering domain d_{XRD}. A lower value of d_{XRD} in the case of P-MoS_2/Al_2O_3 catalyst seems to result from a h igher degree of deformation of MoS_2 slabs, which in turn could have been a reason of higher activity of P-MoS_2/Al_2O_3 catalyst in HDO and HDS reactions.

The effect of Mo loading on the dispersion of sulfide phase and catalytic activity of P-MoS_2/Al_2O_3 catalysts in the rapeseed HDO was also studied. With the increase of Mo loading the activities of P-MoS_2/Al_2O_3 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 MoS_2 edge sites that is caused by the increase of sizes of MoS_2 slabs.

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