Inhibition of SRGO hydrodesulfurization over $CoMo/Al_2O_3$ catalyst: comparison of rapeseed oil and carbon monoxide effects

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Abstract: - Inhibition of SRGO hydrodesulfurization (HDS) in the presence of rapeseed oil (RSO) and carbon monoxide was studied over $CoMo/Al_2O_3$ catalyst at 340 °C, 4.0 MPa, LHSV – 2 h^{-1} and H_2/feed ratio – 600 Nm^3/m^3. It was found that both RSO and CO addition decrease the sulfur content in the products, wherein the HDS rate constant correlates with the CO content in the outlet gas irrespective of the source of CO: addition to the inlet gas or production from rapeseed oil HDO. The effect of CO on the selectivity of HDO/$HDeCO_x$ routes is also observed: the ratio C_{18}/C_{17} is increased with the rising of CO concentration in the feed. The obtained results confirm the major role of CO as the inhibitor of HDS reactions in the presence in the blends with RSO.

Key-Words: - hydrodesulfurization, hydrodeoxygenation, CoMo sulfide catalyst, rapeseed oil, SRGO, co-processing

1 Introduction

The growing demand for transportation fuels from the emerging economies, decrease in available fossil fuel resources and vital tendency to reduce the greenhouse gas emissions have caused ascending interest in the production of liquid transportation fuels from renewable resources [1-5]. Triglyceride-based feedstocks are the efficient sources for the production of aviation and diesel-range fuels because their deoxygenation gives linear hydrocarbons completely compatible with the petroleum-derived one [6-8]. Hydrotreating of triglycerides can be performed in the stand-alone units or via the co-processing of renewable oils and fats with the petroleum-derived middle distillates in the existing refinery [1,3,8-10]. In both cases conventional hydrodesulfurization catalysts are used [10-14]; and oxygen removal over sulfide $Co(Ni)Mo/Al_2O_3$ catalysts occurs via two different pathways simultaneously: direct hydrodeoxygenation (HDO) produces hydrocarbons and H_2O, while decarbonylation/decarboxylation route ($HDeCO_x$) gives hydrocarbons with shorter chain and carbon oxides (CO/CO_2) [15-17].

2 Problem Formulation

The literature data concerning the effect of triglyceride-based stock addition on the activity of $CoMo/Al_2O_3$ catalyst in the hydrodesulfurization of gas oil is rather contradictory. The decrease of activity of $CoMo/Al_2O_3$ catalysts in the HDS of SRGO was observed in the presence of 15% of sunflower oil [18] or 10 wt % of rapeseed oil [19]. In accordance with other results, the addition of 5 wt % palm oil to gas oil results in a decrease of the HDS reaction rate over $CoMo/Al_2O_3$ catalyst, but further increase of vegetable oil content up to 10 wt % did not affect hydrodesulfurization efficiency [20, 21]. As well, there is no common point of view on the reason of HDS activity inhibition by oxygen-containing compounds over sulfide $CoMo/Al_2O_3$ catalyst. According to [22], decanoic acid is the major inhibitor due to competitive adsorption of sulfur compounds on the catalyst surface. The same explanation was proposed for the inhibiting effect of dodecanoic acid; the conclusion was supported by the calculated constants of dodecanoic acid adsorption over CoMo and NiMo sulfide catalysts [18]. In other studies, carbon monoxide, that is one of the main by-products of $HDeCO_x$ route, is proposed as the

inhibitor of the HDS activity of sulfide $CoMo/Al_2O_3$ catalyst [23, 24].

The main goal of the present work is to elucidate the contribution of carbon monoxide to the overall inhibiting effect of rapeseed oil during the co-processing of rapeseed oil and SRGO over sulfide $CoMo/Al_2O_3$ catalyst. In the experiments, the different amounts of rapeseed oil and CO were added to the reaction mixture (SRGO and hydrogen) to correlate the CO content and HDS efficiency over $CoMo/Al_2O_3$ catalyst.

3 Problem Solution

3.1 Experimental

$CoMo/Al_2O_3$ catalyst was prepared by impregnation of alumina granules (BET surface area 208 $m^2 \cdot g^{-1}$, pore volume 0.68 $ml \cdot g^{-1}$, average pore diameter 13.2 nm, purchased by JSK "Promkataliz", Russia) with an aqueous solution containing MoO_3, H_3PO_4, citric acid (all purchased by Vekton, Russia) and cobalt hydroxide (Aldrich, USA); the molar ratio of Co/Mo, P/Mo, and citric acid/Mo was adjusted to 0.5, 0.4 and 0.7, correspondingly. The samples were dried at room temperature and then at 220 °C for 4 hours.

The textural properties of the catalyst were determined using nitrogen physisorption with an ASAP 2400 instrument (USA); the elemental analysis was performed using Optima 4300 DV (Perkin Elmer, France). The morphology of sulfide phase was studied using JEM-2010 transmission electron microscope (JEOL, Japan) with accelerating voltage of 200 kV and resolution of 0.14 nm. The sample was applied to copper gauze in an alcoholic suspension prepared with an ultrasonic disperser. To obtain statistical information, the structural parameters of ca. 500 particles were measured.

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 was diluted by an inert material, carborundum (0.1-0.25 mm size fraction) in a 1:2 volume ratio. The catalyst was sulfided *in situ* prior to the experiment with straight-run diesel fraction containing additionally 0.6 wt % sulfur as dimethyl disulfide (at H_2 pressure 3.5 MPa; H/C – 300 Nm^3/m^3; LHSV – 2 h^{-1}). The sulfidation was performed in two steps: at 240 °C for 8 hours and then at 340 °C for 6 hours. The effect of rapeseed oil on HDS reactions was studied using SRGO-RSO blends containing 5, 10, 15 and 20 wt % of rapeseed oil. Effect of CO was examined by introducing of carbon monoxide (0-3 vol %) into the hydrogen stream. The reactions were carried out at 340 °C under 4.0 MPa with LHSV – 2 h^{-1} and H_2/feed ratio 600 Nm^3/m^3 varying the RSO content in diesel fraction and/or CO content in the gas phase. Liquid feed was supplied using a Gilson 305 liquid chromatography pump; hydrogen was fed using a Bronkhorst automated flow controllers. The duration of each stages differing in condition was 12 hours; the residual sulfur and nitrogen contents were obtained by averaging the data for three samples taken through 10, 11 and 12 hours 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 3500SCl energy dispersive X-ray fluorescence analyzer (Oxford Instruments, United Kingdom). Micro amounts of nitrogen and sulfur in the products were measured on an ANTEK 9000NS nitrogen/sulfur analyzer (Antek Instruments L.P., USA) using the ASTM D 5762 and ASTM D 5453 standard procedures. The total oxygen content in the reaction mixture before and after hydrorefining was determined using a Vario EL Cube CHNSO analyzer (Elementar Analysensysteme GmbH, Germany).

Table 1. The heteroatom amounts in the feed depending on RSO content

	Units	RSO content, wt %				
		0	5	10	15	20
S	wppm	10300	9800	9200	8700	8200
N	wppm	151	150	148	145	141
O	wt %	0.068	0.621	1.15	1.70	2.34

Gas phase was analyzed on-line using a gas chromatograph «Chromos 1000» («Chromos», Russia), equipped with the FID detector. The concentrations of CO and CO_2 were determined in the form of methane after separation on a column packed with 80/100 mesh HayeSep® («Sigma-Aldrich», USA) and subsequent hydrogenation over reduced Pd catalyst at 340 °C.

3.2 Results and discussion

According to chemical analysis, $CoMo/Al_2O_3$ catalyst after calcination at 500 °C contained 13.2 wt % of Mo, 3.9 wt % of Co and 2.1 wt % of P. The TEM image of the sulfided $CoMo/Al_2O_3$ catalyst taken after the reaction is presented in Figure 1.

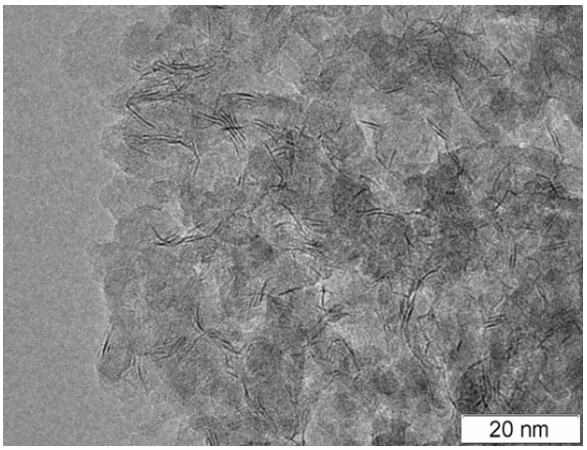

Fig. 1. TEM image of the sulfided $CoMo/Al_2O_3$ catalyst

On the surface of alumina, there are the black thread-like fringes characteristic to the nano-crystalline MoS_2 slab-like structure. The average slab length and stacking number of the sulfide nanoparticles on the catalyst's surface are about 3.1 nm and 1.6, correspondingly. The formation of nickel sulfide (Ni_xS_y) or cobalt sulfide (Co_xS_y) crystallites is not observed. Thus, the formation of highly dispersed sulfide nanoparticles on the surface of the alumina support was confirmed with TEM data.

First of all, it should be noted that the oxygen was not detected in the liquid products by means of Vario El Cube, that points out to the complete conversion of rapeseed oil or intermediate oxygen-containing compounds (ethers, acids, alcohols) in the conditions of the experiments. The resulting sulfur and nitrogen contents in the hydrotreating products depending on rapeseed oil contents in the SRGO are shown in Figure 2. It was shown that sulfur and nitrogen contents are increased sharply when 5 wt % of RSO is added to the SRGO; the further increase of RSO content in the initial feed have a less appreciable effect on the impurities concentrations in the products. Sulfur and nitrogen contents are even decreased slightly in the products obtained from the mixture containing 20 wt % of rapeseed oil.

Previously one of the main by-products of rapeseed oil HDO, carbon monoxide, was proposed as the inhibitor of the HDS reactions over sulfide $CoMo/Al_2O_3$ catalyst [23, 24]. In our experiments, the gradual increase of CO concentrations in the feed was observed with the increase of RSO content in the feed. The sulfur content in the products was increased with the rising of CO content in the gas phase, but only up to 15 wt % of RSO in the feed (Figure 3).

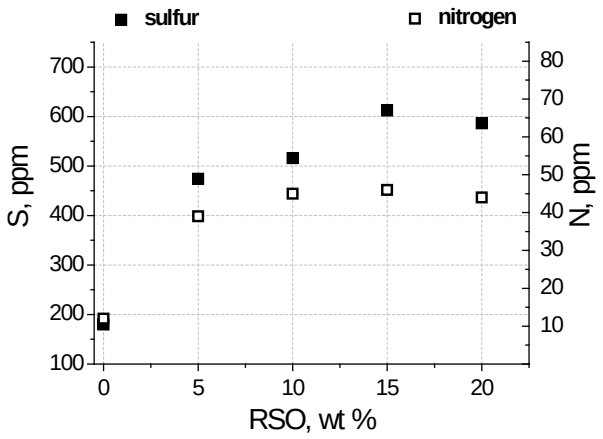

Fig. 2. Sulfur and nitrogen concentrations in the products depending on RSO content in the feed (T – 340 °C, P – 4.0 MPa, H_2/feed – 600 Nm^3 H_2/m^3 feed, LHSV – 2 h^{-1})

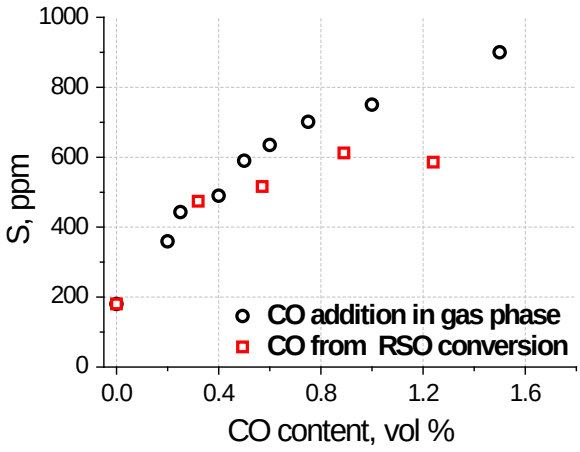

Fig. 3. Dependence of sulfur content in the products on the CO concentrations in the gas phase (T – 340 °C, P – 4.0 MPa, H_2/feed – 600 Nm^3 H_2/m^3 feed, LHSV – 2 h^{-1})

Nearly the same contents of sulfur were produced from the feeds, containing 15 and 20 wt % of RSO despite the appreciable difference in CO content. The tendency is rather different when carbon monoxide is added to the reaction mixture: the gradual increase of sulfur contents in the products are observed with the rising of CO content in the feed clearly demonstrating the inhibiting effect of CO on the HDS reactions (Figure 3). This difference can be explained by the dilution of the sulfur-containing compounds in the feed: the more is the RSO content, the less is the sulfur concentration in the feed. As a consequence, lower concentrations of sulfur in the feeds facilitate HDS, leading to the nearly the same sulfur content in the products of feeds, containing 15 and 20 wt % of RSO. Besides,

the contents of other inhibitors of HDS reaction, such as N-containing compounds, aromatics, and hydrogen sulfide are also decreased with the RSO increase, in contrast with the CO addition to the feed.

So, the dilution of SRGO components by RSO makes impossible the direct comparison of the effect of carbon monoxide obtained in the HDO reactions with that caused by CO addition to the initial feed. To elucidate the contribution of carbon monoxide to the overall inhibiting effect of rapeseed oil during the co-processing of rapeseed oil and SRGO over sulfide $CoMo/Al_2O_3$ catalyst the reaction rate constant k of hydrodesulfurization reactions was used calculated in accordance with the equation (1):

$$\frac{dC_S}{dt} = -k \cdot C_S^n dt \qquad (1)$$

where C_s – sulfur concentration, n – apparent hydrodesulfurization reactions order and t – reaction time. Experimentally estimated value of n was 1.44.

Figure 4 summarizes the dependences of k on carbon monoxide content in the resulting feed for the experiments, differing in CO sources: *a)* hydrotreating of SRGO with the addition of CO in the gas feed; *b)* hydrotreating of SRGO-RSO blends; *c)* hydrotreating of SRGO-RSO blends with the additional CO in the gas phase.

The obtained results show that activity of $CoMo/Al_2O_3$ catalyst in hydrodesulfurization of SRGO correlates well with the CO content in the gas phase irrespective of the source of carbon monoxide: from the addition to gas-phase or from RSO conversion. $CoMo/Al_2O_3$ catalysts demonstrate even slightly better activity (at the same CO content) in the experiments with the rapeseed oil that is explained by the decrease of the contents of inhibitors (H_2S, NH_3, and aromatics) in the SRGO-SRO mixture in comparison with the SRGO. So, the obtained results confirm that CO, not rapeseed oil or intermediate oxygen-containing compounds (ethers, acids, alcohols) plays a decisive role of in the inhibition of HDS reactions during hydrotreatment of SRGO-RSO blends.

The most likely cause of the inhibiting effect of carbon monoxide on HDS activity of the $CoMo/Al_2O_3$ catalyst is the adsorption of CO molecules on active catalyst centers [23, 24]. In such a case, the CO molecules must have also influenced the proceeding the HDO reactions of triglycerides and fatty acids of rapeseed oil as well as the intermediate products of their transformation.

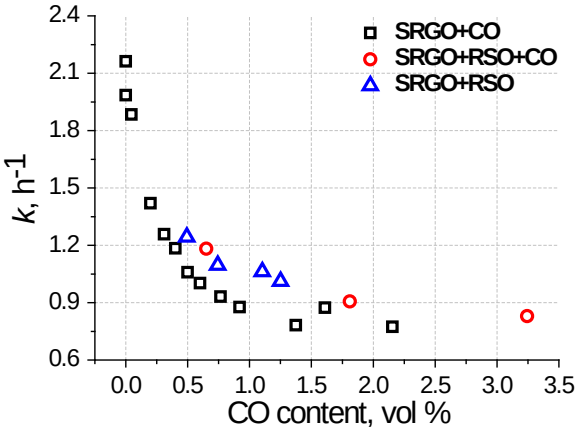

Fig. 4. Rate constants of SRGO desulfurization depending on CO content in the resulting feed (T – 340 °C, P – 4.0 MPa, H_2/feed – 600 Nm^3 H_2/m^3 feed, LHSV – 2 h^{-1})

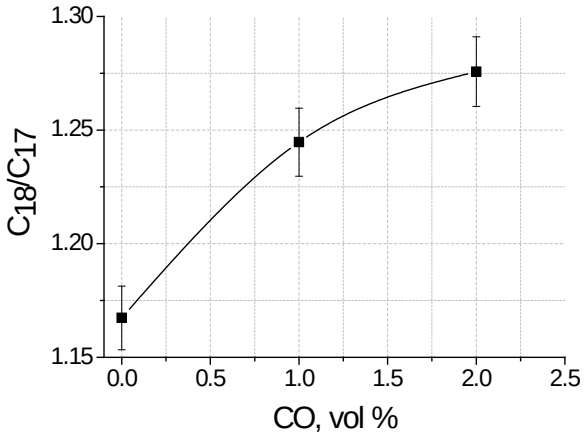

Fig. 5. The impact of CO on the C_{18}/C_{17} ratio in the hydrotreatment of 10 wt % RSO with SRGO over $CoMo/Al_2O_3$ catalyst (T – 340 °C, P – 4.0 MPa, H_2/feed – 600 Nm^3 H_2/m^3 feed, LHSV – 2 h^{-1})

It was assumed, that CO could have blocked to a greater degree the active sites responsible for the hydrogenolysis of the C-C bonds, accompanied by the formation of CO molecules. Figure 5 shows the dependence of C_{18}/C_{17} hydrocarbons ratio in the products of the hydrotreating of RSO-SRGO blend (10 wt % of RSO) on the content of CO, added to the gas phase. From the data presented, it can be seen that the amount of CO in the gas phase affects the selectivity: the contribution of reactions giving C_{18} hydrocarbon (proceeding without the formation of CO) is increased with the rising of CO concentration in the gas phase. Thus, in our experiment, the presence of 1 vol % of CO in the hydrogen feed resulted in the increase of the C_{18}/C_{17} ratio from 1.167 to 1.245.

The observed effect of CO content on the selectivity of HDO/HDeCO$_x$ routes is the indirect indication that the breakdown of C-C and C-O bonds occur on the different types of active sites and the adsorption of CO to a greater degree suppresses the centers at which the C-C bonds are broken.

4 Conclusion

The effect of rapeseed oil and CO on the behavior of CoMo/Al_2O_3 catalysts in HDS of SRGO were studied in the hydrotreating of SRGO at 340 °C under 4.0 MPa with LHSV – 2 h^{-1} and H_2/feed ratio 600 Nm^3/m^3. The different amounts of rapeseed oil and/or CO were added to the reaction mixture (SRGO or hydrogen). It was found that activity of CoMo/Al_2O_3 catalyst in HDS of SRGO correlates with the CO content in the outlet gas irrespective of the source of carbon monoxide that was produced from HDO of rapeseed oil or directly added to the inlet gas. The increase of CO content was accompanied by the decrease of HDS rate constant, especially noticeable in the range up to 1 vol % of CO. The effect of CO content on the selectivity of HDO/HDeCO$_x$ routes is observed: the contribution of HDO routes (with C_{18} hydrocarbon formation) is increased with the rising of CO concentration in the gas phase, indicating that CO suppresses the centers at which the C-C bonds is broken adsorption to a greater degree. The obtained results confirm the major role of CO as the inhibitor of HDS reactions in the triglyceride-containing feedstocks.

Acknowledgments

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