

## Beneficial effect of ethylene glycol on the activity of P-doped NiMo/Al<sub>2</sub>O<sub>3</sub> HDS catalysts

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*Abstract:* - Phosphorous-doped NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst prepared using ethylene glycol (EG) as additive was tested in the hydrotreating of straight-run gas oil. The organic agent was diluted in the impregnation solution obtained by the dissolving of MoO<sub>3</sub> and Ni(OH)<sub>2</sub> in water solution of H<sub>3</sub>PO<sub>4</sub>. The TEM data confirmed that the procedures used in catalyst preparation and sulfidation ensure the formation of highly dispersed NiMoS nanoparticles. As determined by X-ray photoelectron spectroscopy, the addition of EG leads to the formation of sulfide catalyst with a higher dispersion of Mo on the surface. Accordingly, the catalyst with EG is more active in hydrodesulfurization and hydrodenitrogenation of straight-run gas oil than the catalyst prepared without one.

*Key-Words:* - Hydrodesulfurization, NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, ethylene glycol, straight-run gas oil, hydrodenitrogenation

### 1 Introduction

Increasingly stringent transportation fuel specifications and involvement in the processing of heavier crude oil require development of more active hydrodesulfurization (HDS) catalysts [1]. The most industrially used catalysts are CoMo or NiMo systems supported on alumina. At present it is generally accepted that the active phase of hydrotreating catalysts is presented by MoS<sub>2</sub> layered nanoparticles decorated with cobalt or nickel atoms on the edge faces [2]. The dispersion of active metal, sulfidation degree and amount of Co or Ni atoms on the edges of MoS<sub>2</sub> nanoparticles are the essential factors in the preparation of so-called CoMoS or NiMoS active phase [1, 2].

### 2 Problem Formulation

The use of organic modifiers is one of the ways to prepare more active HDS catalysts; as chelating agents and glycol-type additives are used for this purpose [1, 3, 4]. In opposite to citric acid effect on HDS activity, relatively scarce literature deals with the glycol-type additives. Most articles describe the effect of glycols on the activity of CoMo systems using co-impregnation with the solution of active metals and glycols [3-6], or post-treatment of CoMo(P)/Al<sub>2</sub>O<sub>3</sub> systems with triethylene glycol (TEG) or polyethylene glycol (PEG) [7-10]. Just a few reports were found concerning the effect of glycols addition to the impregnation solution on the activity of NiMoP/Al<sub>2</sub>O<sub>3</sub> catalysts [11-13], despite this system is widely used for the HDS of cracked

stock [1] and is a promising candidates for the hydrotreating of gasoil blends with the tryglycerides due to their resistance to inhibition of HDS reaction with O-containing compounds [14]. It was shown, that the glycol-modified catalysts displayed higher activity in the HDS of model compounds [3-6, 9-12] and gasoil fractions [6, 9-12], in toluene hydrogenation [7, 8]. Moreover synergetic effect of glycol-type additives and P was disclosed [4, 10]. It was proposed that glycols hinder the interaction between the active phase precursors and alumina allowing the formation of oxidic precursor with a high Co(Ni)/Mo atomic ratio [3-5, 12, 13]. But the results concerning the effect of glycol addition on the distribution of promoter (Co, Ni) and Mo species, as well as their sulfidability is rather contradictory. So, according to [3], both dispersions of Co, Mo and ratio of Co and Mo in sulfide state are increased in the sulfide NiMoP/Al<sub>2</sub>O<sub>3</sub> catalysts when ethylene glycol (EG), diethylene glycol and TEG are added to impregnating solution. Using the result of XPS study of dried NiMoP/Al<sub>2</sub>O<sub>3</sub> systems authors [11] have come to the conclusions, that the addition of PEG to the solution led to the increase of Ni dispersion in the dried NiMoP/Al<sub>2</sub>O<sub>3</sub> system, but has no effect on Mo distribution. The sulfided samples were not studied in this work. Using the similar precursors and XPS method for catalyst characterization the authors [12] observed the decrease of Mo dispersion and increase of Ni dispersion in the sulfided NiMoP/Al<sub>2</sub>O<sub>3</sub> after addition of TEG in the solution.

In this work, the effect of EG on Ni and Mo dispersion in the oxide (after drying at 110°C) and sulphide NiMoP/Al<sub>2</sub>O<sub>3</sub> catalysts (after liquid-phase sulfidation and HDS reaction) was studied using XPS method. The non-modified and EG-modified systems were tested in the HDS of straight-run gas oil (SRGO) to estimate the influence of EG on the catalytic properties of P-doped NiMo/Al<sub>2</sub>O<sub>3</sub> materials.

### 3 Problem Solution

#### 3.1 Experimental

The NiMoP/Al<sub>2</sub>O<sub>3</sub> catalysts were prepared by the incipient wetness impregnation of  $\gamma$ -alumina granules with a trilobe cross-section of 1.2 mm and length of 4-6 mm (BET surface area 235 m<sup>2</sup> g<sup>-1</sup>, pore volume 0.79 ml g<sup>-1</sup>, average pore diameter 13.4 nm, purchased by JSK "Promkataliz", Ryazan, Russia) with an aqueous solution containing Ni, Mo, P with and without EG at molar ratios Ni/Mo = 0.4, P/Mo = 0.4 and EG/Mo = 0 or 0.75. Catalysts were denoted as NiMoP/Al<sub>2</sub>O<sub>3</sub> and NiMoP/Al<sub>2</sub>O<sub>3</sub>-EG, correspondingly. Molybdenum (VI) oxide MoO<sub>3</sub> (chemically pure grade, Vekton, Russia), nickel (II) hydroxide Ni(OH)<sub>2</sub> (for analysis, Acros Organics), phosphoric acid H<sub>3</sub>PO<sub>4</sub> (special-purity grade, Vekton, Russia), ethylene glycol (99.5%, Acros Organics) were used as the initial compounds. After impregnation, the samples were dried at 110°C for 4 h. The Ni, Mo and P content in the catalysts after calcination at 550 °C and textural characteristics of the sulfided catalysts are presented in Table 1.

**Table 1.** The physico-chemical characteristics of the catalysts.

Catalyst	NiMoP/Al <sub>2</sub> O <sub>3</sub>	NiMoP/Al <sub>2</sub> O <sub>3</sub> -EG
Mo <sup>a</sup> , wt. %	13.4	13.1
Ni <sup>a</sup> , wt. %	3.4	3.4
P <sup>a</sup> , wt. %	2.0	1.9
S <sub>BET</sub> <sup>b</sup> , m <sup>2</sup> g <sup>-1</sup>	114	120
V <sub>pore</sub> <sup>b</sup> , cm <sup>3</sup> g <sup>-1</sup>	0.34	0.36
D <sub>pore</sub> <sup>b</sup> , nm	11.8	11.9

<sup>a</sup> The content of the elements was determined after calcination of the samples at 550°C for 4 h.

<sup>b</sup> Textural properties are given for catalysts after sulfidation.

The chemical analysis was performed using atomic absorption spectroscopy on an Optima 4300 DV instrument (Perkin Elmer). Textural characteristics were determined from low-temperature nitrogen adsorption isotherms (77 K) obtained on a Micromeritics ASAP 2400 analyzer. The transmission electron microscopy (TEM) studies were carried out using a JEM-2010 electron

microscope (JEOL) with a lattice resolution of 0.14 nm and a 200 kV accelerating voltage. The average size of the NiMoS nanoparticles and the average number of layers per particle were determined by counting over 300 particles in TEM images taken with medium magnification.

X-ray photoelectron spectra (XPS) were recorded on a SPECS (Germany) photoelectron spectrometer using a hemispherical PHOIBOS-150-MCD-9 analyzer (Al K $\alpha$  radiation,  $h\nu = 1486.6$  eV, 200 W). The samples in the form of a powder were loaded onto a conducting double-sided copper scotch. The Al2p peak ( $E_b = 74.5$  eV) corresponding to Al<sup>3+</sup> from Al<sub>2</sub>O<sub>3</sub> support was used as an internal reference [15]. The atomic concentration ratios of elements on the catalyst surface were calculated from the integral photoelectron peak intensities (Al2p, P2p, Mo3d, Ni2p and S2s), which were corrected with theoretical sensitivity factors based on the Scofield's photo-ionization cross sections [16]. The differences in the binding energies for each catalyst did not exceed 0.1 eV, and the discrepancies in the atomic ratios for the elements were not more than 15%.

The catalytic experiments were performed in a trickle-bed down-flow reactor with an inner diameter of 16 mm and length of 570 mm as described in [17]. In each experiment, 10 ml of catalyst (granule length of 4-5 mm) 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 gas oil containing additionally 0.6 wt % sulfur as dimethyl disulfide (H<sub>2</sub> pressure 3.5 MPa; H/C – 300 Nm<sup>3</sup>/m<sup>3</sup>; LHSV – 2 h<sup>-1</sup>). The sulfidation was performed in two steps: at 240 °C for 8 hours and then at 340 °C for 6 hours. The feedstock was straight-run gas oil containing 0.88 wt.% S, 110 ppm N, total aromatic content of 28.0 wt.% (19.2 wt.% of monoaromatics, 7.1 wt.% of diaromatics and 1.7 wt.% of polyaromatics).

The catalytic experiments were performed at temperature of 330 and 340 °C, hydrogen pressure of 3.5 MPa, H<sub>2</sub>/feedstock ratio of 300 Nm<sup>3</sup> hydrogen/m<sup>3</sup> feedstock and liquid hourly space velocity of 2 h<sup>-1</sup>. The duration of each stages differing in condition was 12 hours; the residual sulfur content was 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 hydrogenated products was measured on a Lab-X 3500SCL energy dispersive X-ray fluorescence analyzer (Oxford Instruments, UK) and on an ANTEK 9000NS analyzer (Antek Instruments L.P., USA) for products containing less than 100

ppm S. The nitrogen content was determined using an ANTEK 9000NS.

To measure of HDS activity, the reaction rate constant ( $k$ ) was calculated via a first-order rate equation:

$$\frac{k(n-1)}{W} = \frac{1}{[S]^{n-1}} - \frac{1}{[S_0]^{n-1}}$$

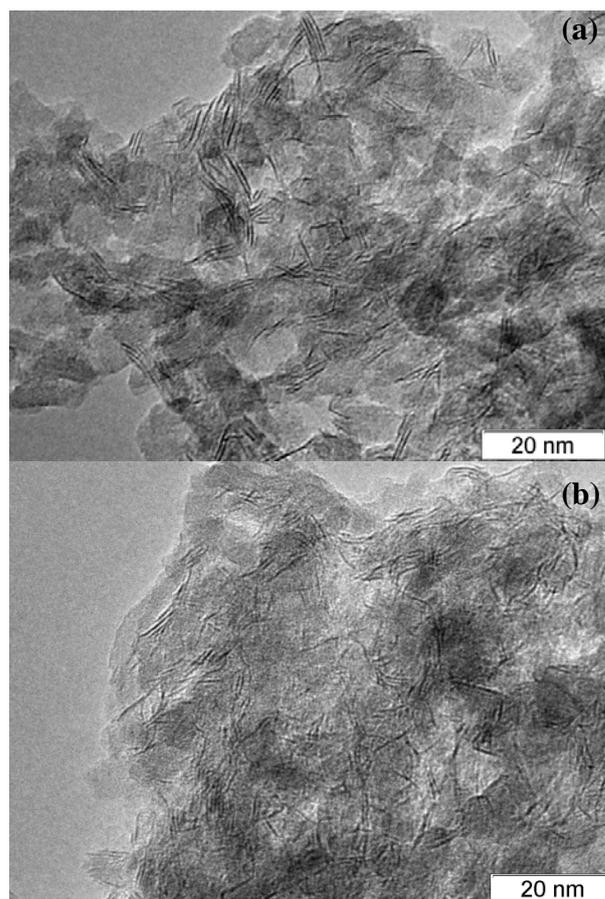
where  $W$  is the feedstock hourly space velocity ( $(\text{m}^3 \text{ feed}) (\text{m}^3 \text{ catalyst})^{-1} \text{ min}^{-1}$ ),  $[S]$  and  $[S_0]$  is the sulfur content of the hydrogenated products and feedstock (wt. %), respectively, and  $n = 1.6$  [17].

### 3.2 Results and discussion

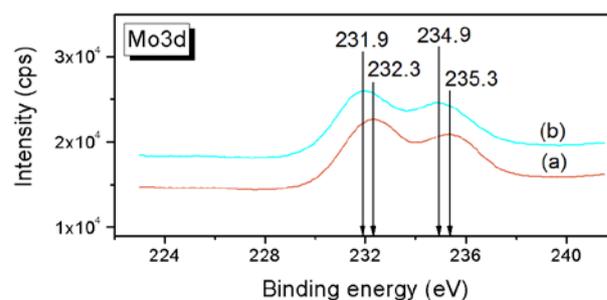
The prepared catalysts contained approximately the same amount of Mo with the Ni/Mo molar ratios of 0.4 and had similar textural properties (Table 1). The TEM images of the sulfided catalysts are presented in Fig. 1. The average particle size determined by statistical processing of the TEM images is 4.7–4.9 nm, and the average number of layers per particle is less than 2. The morphology of the samples is typical of NiMo/Al<sub>2</sub>O<sub>3</sub> sulfide catalysts and corresponds to the structure of molybdenum disulfide MoS<sub>2</sub>. The Ni<sub>x</sub>S<sub>y</sub> crystallites were not observed. Thus, the TEM data give the evidence that the procedures used in catalyst preparation and sulfidation ensure the formation of highly dispersed NiMoS nanoparticles.

To elucidate the effect of EG addition on nickel and molybdenum dispersions in the dried catalysts and to follow the evolution of their dispersion after sulfidation NiMoP/Al<sub>2</sub>O<sub>3</sub> and NiMoP/Al<sub>2</sub>O<sub>3</sub>-EG catalysts in oxide and sulphide forms were characterized by XPS method (Fig. 2–4 and Table 2, 3). Sulfidation degree was also estimated from the XPS spectra of sulfided catalysts.

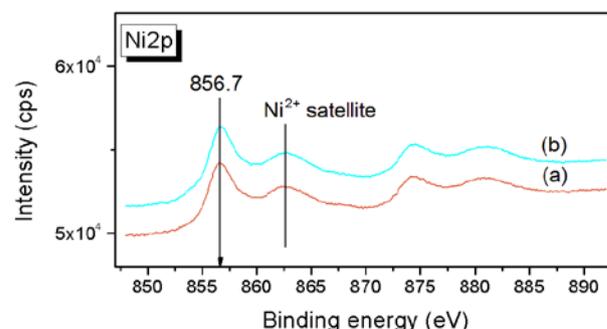
The Mo3d and Ni2p XPS spectra of NiMoP/Al<sub>2</sub>O<sub>3</sub> and NiMoP/Al<sub>2</sub>O<sub>3</sub>-EG catalysts in oxide form (after drying at 110°C) are shown in Fig. 2 and 3. The Mo3d spectrum of NiMoP/Al<sub>2</sub>O<sub>3</sub> contain Mo3d<sub>5/2</sub> and Mo3d<sub>3/2</sub> doublet with a binding energy of 232.3 and 235.3 eV, which can be attributed to Mo<sup>6+</sup> in oxide compound [3]. The spectrum of NiMoP/Al<sub>2</sub>O<sub>3</sub>-EG sample shows a slightly lower the binding energies (231.9 and 234.9 eV) for Mo3d<sub>5/2</sub> and Mo3d<sub>3/2</sub> peaks. This can be explained by partial reduction of Mo<sup>6+</sup> to Mo<sup>5+</sup> during drying in the presence of EG. The binding energy for Ni2p is 856.7 ± 0.1 eV (Fig. 3), which is characteristic of Ni<sup>2+</sup> in the composition of nickel hydroxide [18].



**Fig 1.** TEM images of sulfided catalysts: (a) NiMoP/Al<sub>2</sub>O<sub>3</sub> and (b) NiMoP/Al<sub>2</sub>O<sub>3</sub>-EG.



**Fig 2.** XPS Mo3d spectra of the catalysts in oxide form: (a) NiMoP/Al<sub>2</sub>O<sub>3</sub> and (b) NiMoP/Al<sub>2</sub>O<sub>3</sub>-EG.



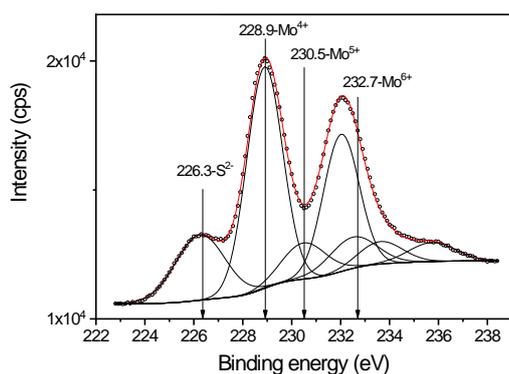
**Fig 3.** XPS Ni2p spectra of the catalysts in oxide form: (a) NiMoP/Al<sub>2</sub>O<sub>3</sub>, (b) NiMoP/Al<sub>2</sub>O<sub>3</sub>-EG.

The chemical surface composition of the catalysts and Ni/Al, Mo/Al and P/Al ratios were estimated from the XPS spectra using the procedure described in section 3.1. It is seen, that EG addition to the impregnation solution has a minor effect on the Mo/Al and P/Al ratio, but the Ni/Mo ratio is increased noticeably, from 0.042 to 0.050 (Table 2). As a result, the use of EG in the course of NiMoP/Al<sub>2</sub>O<sub>3</sub> catalyst preparation induces the increase of Ni/Mo ratio from 0.39 to 0.45. So, the EG provides the increase of Ni dispersion in the dried samples coinciding with the results, obtained in [11].

**Table 2.** XPS data for the catalysts in oxide form.

Catalyst	Ni/Al	Mo/Al	P/Al	Ni/Mo
NiMoP/Al <sub>2</sub> O <sub>3</sub>	0.042	0.11	0.11	0.39
NiMoP/Al <sub>2</sub> O <sub>3</sub> -EG	0.050	0.11	0.10	0.45

The Mo3d spectra of the catalysts in the sulfided form contain the Mo 3d<sub>5/2</sub> and 3d<sub>3/2</sub> doublet with binding energy at 228.9 and 232.1 eV (Fig. 4). The peak with a binding energy of 226.3 eV is assigned to S2s [3, 12]. The data obtained from decomposition of Mo3d spectra [19] are sufficiently similar for both catalysts. The content of each Mo state is within following limits, %: Mo<sup>4+</sup> – 74.5 ± 1.4; Mo<sup>5+</sup> – 14.6 ± 0.3; Mo<sup>6+</sup> – 11.0 ± 1.6. Consequently, sulfidation degree for both catalysts is similar. The Mo/Al atomic ratio obtained from the XPS spectra showed that surface concentration of Mo is 2 times higher for NiMoP/Al<sub>2</sub>O<sub>3</sub>-EG catalyst as compared with NiMoP/Al<sub>2</sub>O<sub>3</sub> (Table 3).



**Fig 4.** XPS Mo3d spectrum of the NiMoP/Al<sub>2</sub>O<sub>3</sub>-EG catalyst in the sulfided state.

The catalytic properties of the NiMoP/Al<sub>2</sub>O<sub>3</sub> and NiMoP/Al<sub>2</sub>O<sub>3</sub>-EG catalysts were compared in the hydrotreating of straight-run gas oil. The catalyst prepared using EG shows a higher

hydrodesulfurization activity than the catalyst prepared without the additive (Table 4).

**Table 3.** XPS data for the catalysts in the sulfided state.

Catalyst	Ni/Al	Mo/Al	P/Al	S/Ni+Mo
NiMoP/Al <sub>2</sub> O <sub>3</sub>	0.05	0.07	0.10	1.40
NiMoP/Al <sub>2</sub> O <sub>3</sub> -EG	0.04	0.14	0.11	1.43

A comparison between the HDS rate constants (*k*) for NiMoP/Al<sub>2</sub>O<sub>3</sub> and NiMoP/Al<sub>2</sub>O<sub>3</sub>-EG catalysts demonstrates that the introduction of EG in the impregnation solution increases the activity of the catalyst at 330 and 340 °C by a factor of 2.1 and 1.9, respectively. The hydrodenitrogenation (HDN) activity is also higher in the presence of NiMoP/Al<sub>2</sub>O<sub>3</sub>-EG catalyst, as is indicated by the lower nitrogen content of the resulting hydrogenated products. These results can be explained by the influence of EG on the Mo concentration on the catalyst surface (Table 3). Accordingly, the NiMoP/Al<sub>2</sub>O<sub>3</sub>-EG catalyst is more active in HDS and HDN of straight-run gas oil than NiMoP/Al<sub>2</sub>O<sub>3</sub> with lower surface concentrations of Mo.

**Table 4.** Catalytic properties of the NiMo(P)/Al<sub>2</sub>O<sub>3</sub> catalysts in the hydrotreating of SRGO.

Catalyst	T, °C	S, ppm	N, ppm	<i>k</i> *10 <sup>3</sup> , min <sup>-1</sup> ppm <sup>-0.6</sup>
NiMoP/Al <sub>2</sub> O <sub>3</sub>	330	340	19	0.52
NiMoP/Al <sub>2</sub> O <sub>3</sub>	340	166	15	0.85
NiMoP/Al <sub>2</sub> O <sub>3</sub> -EG	330	109	11	1.11
NiMoP/Al <sub>2</sub> O <sub>3</sub> -EG	340	60	6	1.63

The apparent activation energy for SRGO hydrodesulfurization (within the temperature range from 330 to 340 °C) estimated from the slope of the Arrhenius plot was in the range of 120 to 145 kJmol<sup>-1</sup>. Therefore, there is no influence of external or internal mass transfer limitations under the conditions used.

#### 4 Conclusion

The addition of EG to the impregnation solution obtained by the dissolving of MoO<sub>3</sub> in H<sub>3</sub>PO<sub>4</sub> aqueous solution followed by Ni(OH)<sub>2</sub> addition allowed us to prepare a more active NiMo/Al<sub>2</sub>O<sub>3</sub> hydrotreating catalyst. The catalyst with EG is about 2 times more active in HDS of straight-run gas oil than the catalyst prepared without one. This can be explained by the promoting influence of ethylene glycol on the dispersion of Mo in the sulfide catalyst. In future, it will be interesting to compare

the effect of other glycol-type molecules, differing in molecular mass, boiling point and viscosity, on the catalytic properties of P-doped CoMo and NiMo catalysts.

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