NiMo/ γ -Al₂O₃ Catalysts from Ni Heteropolyoxomolybdate and Effect of Alumina Modification by B, Co, or Ni

Radostina PALCHEVA¹, Luděk KALUŽA^{2,*}, Alla SPOJAKINA¹, Květuše JIRÁTOVÁ², Georgi TYULIEV¹

¹*Institute of Catalysis, Bulgarian Academy of Sciences, G. Bonchev str., bldg. 11, 1113 Sofia, Bulgaria*

²*Institute of Chemical Process Fundamentals of the Academy of Sciences of the Czech Republic, v.v.i., 165 02 Prague 6, Czech Republic*

Abstract: A hydrotreating NiMo/ γ -Al₂O₃ catalyst (12 wt% Mo and 1.1 wt% Ni) was prepared by impregnation of the support with the Anderson-type heteropolyoxomolybdate (NH₄)₄Ni(OH)₆Mo₆O₁₈. Before impregnation of the support, it was modified with an aqueous solution of H₃BO₃, Co(NO₃)₂, or Ni(NO₃)₂. The catalysts were investigated using N₂ adsorption, O₂ chemisorption, X-ray diffraction, UV-Vis spectroscopy, Fourier transform infrared spectroscopy, temperature-programmed reduction, temperature-programmed desorption, and X-ray photoelectron spectroscopy. The addition of Co, Ni, or B influenced the Al₂O₃ phase composition and gave increased catalytic activity for 1-benzothiophene hydrodesulfurization (HDS). X-ray photoelectron spectroscopy confirmed that the prior loading of Ni, Co or B increased the degree of sulfidation of the NiMo/ γ -Al₂O₃ catalysts. The highest HDS activity was observed with the NiMo/ γ -Al₂O₃ catalyst with prior loaded Ni.

Key words: nickel; cobalt; boron; nickel heteropolyoxomolybdate; hydrodesulfurization

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*Corresponding author. Tel: +420-220390293; Fax: +420-220390111; E-mail: kaluza@icpf.cas.cz

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Sulfur compounds that are present in fuel would poison catalytic converters, which would generate polluting emissions. Therefore, there are regulations that limit the sulfur content in fuels. The production of fuel to meet these regulations will require new more effective catalysts. Supported Co(Ni) and Mo catalysts are extensively used in hydrotreating processes for the production of environmentally friendly fuels, and these catalysts have been extensively studied [1]. The nature of the support plays an important role in the morphology and dispersion of the active phases and catalytic activity of the catalysts [2]. A synergistic effect between the support and the NiMo hydrodesulfurization (HDS) catalyst has been proposed [3].

Various supports have been studied for hydrotreating catalysts. The most widely used support remains alumina because of its excellent mechanical and dispersion properties [4]. Usually, the active components are loaded onto the support using Co(Ni) nitrates and ammonium heptamolybdate solutions, and the best promoting effect of Co(Ni) is at a Co(Ni)/(Co(Ni)+Mo) ratio of 0.3–0.6 [5]. Despite the research of the last decade, the promoting role of Co, Ni, and the support remains unclear. Previous studies have shown that the use of heteropolyoxomolybdate in the preparation of HDS catalysts may provide an interesting alternative to

traditional systems [6,7]. It has been shown that the use of ammonium salts (e.g., of CoMo₆O₂₄H₆ or NiMo₆O₂₄H₆) gave a higher HDS activity at a lower Co(Ni)/(Co(Ni)+Mo) molar ratio (0.14), and Anderson-type heteropolycompounds were effective precursors for the multilayered active phase of hydrotreating catalysts [8–13]. The HDS and hydrogenation (HYD) activities depend on the nature of the heteroatom [14].

Various methods of catalyst modification are applied to improve the catalytic performance of CoMo and NiMo catalysts, and to elucidate the effect of support properties on HDS activity. Various additives can be used to modify the properties of the support but contradictory results have been reported in the literature regarding their effects on the properties of the alumina support and the HDS catalyst. Li et al. [15] found a correlation between acidity and HDS activity for CoMo/alumina-aluminum borate catalysts and a beneficial effect on the acidity and metal dispersion upon addition of boron. Ramirez et al. [16] have shown that the promotional effect of boron on HDS activity reached its maximum at a content of 0.8 wt%. In contrast, Perez-Martinez et al. [17] found a decrease in HDS activity in a study of the effect of the acid-base characteristics of alumina (γ -Al₂O₃) modified with B, Na, or K used for diesel hydrotreatment.

This may be due to changes in the distribution of Co and Mo species in the oxide state. Lafitau et al. [18] observed a lower interaction between the loaded metals and alumina in the presence of boron. On the other hand, Houalla and Delmon [19] reported that the addition of boron promoted the interaction between cobalt and alumina in CoMo/Al₂O₃ catalysts. Giraldo and Centeno [20] reported that CoMo and NiMo supported on alumina modified by different quantities of B₂O₃ (4–14 wt%) did not change the HDS activity at low boron contents. The NiMo catalysts showed slightly higher activity than the CoMo catalysts.

Recently we showed that alumina modified with various amounts of Co prior to the deposition of cobalt heteropolyoxomolybdate up to a molar ratio of Co/Mo = 0.27 substantially increased the activity for the HDS of thiophene and 1-benzothiophene (BT) [21]. The aim of this paper is to study the influence of Ni, Co or B modification of the alumina support on the properties and HDS activity of NiMo/ γ -Al₂O₃ catalysts prepared using Anderson-type Ni heteropolyoxomolybdate. The activity was studied for the HDS of BT.

1 Experimental

1.1 Catalyst preparation

The NiMo catalysts were prepared using a commercial γ -Al₂O₃ support (A_{BET} = 200 m²/g, total volume of pore = 0.40 cm³/g, average radius of the pores = 3.2 nm, particle size fraction = 0.16–0.32 mm). The support was impregnated with an aqueous solution of the ammonium salt of nickel heteropolyoxomolybdate, (NH₄)₄Ni(OH)₆Mo₆O₁₈ (NiMo₆), which was synthesized according to reference [22]. The catalyst had 12 wt% Mo and 1.1 wt% Ni. Impregnation with nickel heteropolyoxomolybdate was performed in a vacuum evaporator at 70 °C. The impregnated support was dried for 4 h at 105 °C and calcined for 2 h at 350 °C. This catalyst is referred to as NiMo₆/Al (unmodified alumina support).

Three other HDS catalysts were prepared by the addition of H₃BO₃, Co(NO₃)₂, and Ni(NO₃)₂ to the alumina support prior to the loading of the NiMo₆ salt. First, the alumina support was impregnated with an aqueous solution of the nitrates or boric acid in a vacuum evaporator for 1 h. The modified support was dried for 4 h at 105 °C and calcined in air for 2 h at 350 °C with a heating rate of 1.7 °C/min. Then the modified support was impregnated with an aqueous solution of the ammonium salt of nickel heteropolyoxomolybdate and thermally treated for 2 h in air at 350 °C. The catalysts with B, Co, and Ni modifications of the alumina support are referred as NiMo₆/Al-B, NiMo₆/Al-Co, and NiMo₆/Al-Ni, respectively.

1.2 Catalyst characterization

The metal contents in the catalysts were determined by chemical analysis (atomic absorption spectroscopy). The surface area and pore size distribution were determined by nitrogen adsorption at –195 °C using a Micromeritics ASAP 2010. The samples were first dried at 105 °C and evacuated at 350 °C (approximately 2–5 h). The data were treated by the standard BET method to calculate the specific surface area (A_{BET}). The mesoporous surface area (A_{meso}) and volume of the micropores (V_{micro}) were determined from t -plot method. The total pore volume (V_{tot}) was calculated from the amount of N₂ adsorbed at $p/p_0 = 0.98$. The pore radius (R) was determined from the pore size distribution evaluated based on the adsorption branch of the adsorption–desorption isotherm.

The X-ray diffraction measurements were performed using a Bruker AXS 2D Powder XRD analyzer with filtered Cu K_{α} radiation at 30 kV acceleration with a 10 mA current. Infrared spectra of the samples mixed with 1 wt% KBr were recorded on a Nicolet 6700 FT-IR spectrophotometer (Thermo Fisher Scientific, USA). The spectra were taken in the region of 400–4000 cm^{–1} at 0.4 cm^{–1} resolution using 50 scans. Alumina absorption in the 400–1200 cm^{–1} range was compensated for by the subtraction of a normalized spectrum of the equivalent amount of support from the spectra of the catalysts. The DR UV-Vis spectra were taken with a Thermo Evolution 300 spectrometer equipped with a Praying Mantis diffuse reflectance accessory.

Temperature-programmed reduction (TPR) measurements of the calcined samples (0.025 g) were performed with an H₂/N₂ mixture (10 mol% H₂) and a flow rate of 50 ml/min with a linear temperature increase of 20 °C/min up to 1000 °C [21]. During the TPR measurement, reduction of the ground CuO (0.16–0.315 mm) was performed to calibrate the absolute values of the hydrogen consumed during the reduction. Temperature-programmed desorption (TPD) of NH₃ was measured with a 0.050 g sample at 20–1000 °C with a helium carrier gas. Ten doses of ammonia were fed to the catalyst sample at 30 °C before flushing the sample with helium for 1 h and heating with a ramp rate of 20 °C/min. The mass spectra using (m/z) 2-H₂ and 16-NH₃ were collected using a Balzers Omnistar mass spectrometer.

Oxygen chemisorption was performed over presulfided catalysts (details on the sulfidation procedure is provided in Section 2.3) flushed by helium (Linde 6.0) at 400 °C for 1 h and then cooled in a mixture of dry ice and ethanol. The amount of chemisorbed oxygen was determined from pulses of O₂ using a thermal conductivity detector, VICI valves (Valco Instrument Inc., USA), and a HP 3394A integrator (Hewlett Packard).

X-ray photoelectron spectroscopy (XPS) measurements

were obtained with an ESCALAB-MK II (VG Scientific) electron spectrometer with a base pressure of $\sim 5.10\text{--}8\text{ Pa}$. The samples were excited with Al K_{α} radiation ($h\nu = 1486.6\text{ eV}$). The energy resolution of the instrument was 1.2 eV as measured by the FWHM of the Ag $3d_{5/2}$ photoelectron line. Powdered sulfided samples (details on the sulfidation procedure are provided in Section 2.3) were transferred into the holders without exposure to air in a glove box connected to the fast entry lock of the XPS instrument. The following photoelectron lines were recorded: C $1s$, O $1s$, Mo $3d$, Co $2p$, Ni $2p$, B $1s$, Mo $3p$, and S $2p$. All binding energies were referenced to the C $1s$ photoelectron line centered at 285.0 eV . The surface atom concentrations were obtained using the photoelectron peak areas divided by the corresponding sensitivity factors taken from [23].

1.3 HDS of BT

HDS of BT was performed in the gas phase using an integral fixed bed tubular flow microreactor (i.d. 3 mm) at $360\text{ }^{\circ}\text{C}$ and 1.6 MPa . Prior to the measurements, the catalysts were presulfided at $400\text{ }^{\circ}\text{C}$ in situ in a $\text{H}_2\text{S}/\text{H}_2$ flow ($1/10$) and atmospheric pressure with a temperature ramp of $10\text{ }^{\circ}\text{C}/\text{min}$ and a dwell time of 1 h . The composition of the feed was 16, 200, and 1384 kPa of BT, decane, and hydrogen, respectively. The catalyst sample (0.04 g) was diluted with inert $\alpha\text{-Al}_2\text{O}_3$ with a particle size fraction of $0.16\text{--}0.32\text{ mm}$ to form a bed length of 30 mm . To avoid mass diffusion limitation, the most active catalyst was crushed to a particle size fraction of $0.08\text{--}0.16\text{ mm}$ and diluted with the $\alpha\text{-Al}_2\text{O}_3$. The measurement confirmed that the experimental conditions were under kinetic control. The reaction was run at three feed rates of BT of 7.7, 10.3, and 15.5 mmol/h . Steady state was reached in 30 min after each change in the feed rate. Deactivation of the catalyst during the catalytic measurements was not observed. The product mixture was analyzed on a Hewlett-Packard gas chromatograph (6890 series) equipped with a capillary column (HP-5, $30\text{ m} \times 0.53\text{ mm} \times 1.5\text{ }\mu\text{m}$). Dihydrobenzothiophene (DH) and ethylbenzene (EB) were identified in the reaction products. The relative compositions (a_{BT} , a_{EB} , and a_{DH}) and conversions (X_{BT} , X_{EB} , and X_{DH}) were defined as $a_{\text{BT}} = (1 - X_{\text{BT}}) = n_{\text{BT}}^0/n_{\text{BT}}$, $a_{\text{EB}} = X_{\text{EB}} = n_{\text{EB}}/n_{\text{BT}}^0$, $a_{\text{DH}} = X_{\text{DH}} = n_{\text{DH}}/n_{\text{BT}}^0$, where n_{BT}^0 , n_{BT} , n_{EB} , and n_{DH} were the initial number of moles of

BT, and final number of moles of BT, EB, and DH, respectively.

2 Results and discussion

2.1 Chemical analysis and porous structure

The chemical analysis of the synthesized initial salt (synthesized in our laboratory) showed the composition of $46.25\text{ wt\% Mo}$ and $4.25\text{ wt\% Ni}$. The molar ratio of Ni/Mo in the initial salt was 0.15. The concentration of Mo in the catalyst was $12\text{ wt\%}$. The catalyst composition is presented in Table 1. The data in Table 1 showed a partial loss of the alumina surface ($200\text{ m}^2/\text{g}$) after loading the NiMo_6 salt. This result can be explained by a partial blockage of the mesopores because they contribute most to the total surface. However, the modification of $\gamma\text{-Al}_2\text{O}_3$ with Co, Ni, and B did not significantly influence the textural parameters of the NiMo_6/Al catalysts. The surface area and volume of micropores were slightly higher for the $\text{NiMo}_6/\text{Al-Ni}$ catalyst compared with the others. In addition, the mesoporous surface area and mesopore radii were slightly higher for the $\text{NiMo}_6/\text{Al-Ni}$ and $\text{NiMo}_6/\text{Al-B}$ catalysts.

2.2 XRD analysis

The XRD patterns of the alumina-supported NiMo catalysts are shown in Fig. 1. Wide-angle XRD patterns of the NiMo catalysts in their oxide form were very diffused. Nevertheless, the diffraction patterns of cubic $\gamma\text{-Al}_2\text{O}_3$ with primary 2θ peaks at 46° and 67° (JCPDS 10-425) could be distinguished in all the samples. The NiMo_6/Al , $\text{NiMo}_6/\text{Al-Co}$, and $\text{NiMo}_6/\text{Al-B}$ catalysts exhibited the presence of the crystalline orthorhombic phase of MoO_3 with the principal reflection at 27.3° . At the calcination temperature of $350\text{ }^{\circ}\text{C}$, MoO_3 in the crystalline form should occur in the orthorhombic (stable between 330 and $740\text{ }^{\circ}\text{C}$) and probably also in the monoclinic (stable between 17 and $330\text{ }^{\circ}\text{C}$) structures. However, no crystalline phase of MoO_3 was found for the $\text{NiMo}_6/\text{Al-Ni}$ catalyst, which showed its Mo species were highly dispersed either in the form of amorphous particles or as crystallites smaller than 4 nm . The absence of the characteristic reflections of NiO oxides ($2\theta = 43.5^{\circ}$ and 63.0°) in the diffraction pattern of the NiMo

Table 1 Composition, specific surface area, and porous characteristics of the catalysts

Sample	Additive (mg/g)	(Ni+Ad)/Mo (mol/mol)	$A_{\text{BET}}/(\text{m}^2/\text{g})$	$V_{\text{tot}}/(\text{cm}^3/\text{g})$	$A_{\text{meso}}/(\text{m}^2/\text{g})$	R/nm	$V_{\text{micro}}/(\text{mm}^3/\text{g})$
$\gamma\text{-Al}_2\text{O}_3$	0.00	—	200	0.40	—	3.2	—
NiMo_6/Al	0.00	0.15	126	0.36	75	4.3	29
$\text{NiMo}_6/\text{Al-Co}$	12.60	0.31	132	0.36	64	4.2	31
$\text{NiMo}_6/\text{Al-B}$	12.42	1.06	123	0.31	75	4.9	30
$\text{NiMo}_6/\text{Al-Ni}$	12.48	0.32	143	0.36	79	4.5	34

Fig. 1. XRD patterns for the supported NiMo₆ catalysts. (1) NiMo₆/Al-B; (2) NiMo₆/Al-Ni; (3) NiMo₆/Al-Co; (4) NiMo₆/Al.

catalysts suggested that these NiO compounds were amorphous or microcrystalline. The identification of NiAl₂O₄ spinel was difficult, particularly at low content of NiAl₂O₄, because the diffraction peaks of γ -Al₂O₃ and NiAl₂O₄ ($2\theta = 31.4^\circ, 37^\circ, 45^\circ, 65.5^\circ$) overlap.

2.3 IR spectra

The IR spectra of the catalysts are shown in Fig. 2. Four broad bands at 440, 665, 890, and 945 cm⁻¹ were observed. The IR spectra of the catalysts were very similar but exhibited small differences. The bands at 440, 665, 890, and 945 cm⁻¹ were assigned to the vibrations of the Mo–O–Mo bridging bonds ($\nu_{as} = 650$ cm⁻¹, $\nu_s = 450$ cm⁻¹) [24] and the bands at 880–950 cm⁻¹ to the *cis*-MoO₂ bonds [25]. In the spectra of the samples prepared with the modified supports, a small shift in the bands to higher frequencies and a higher ratio of the 890 and 945 cm⁻¹ band intensities were observed, especially with the NiMo₆/Al-Ni and NiMo₆/Al-B

Fig. 2. IR spectra of the calcined NiMo₆ catalysts. (1) NiMo₆/Al-B; (2) NiMo₆/Al-Ni; (3) NiMo₆/Al-Co; (4) NiMo₆/Al.

catalysts. The increased intensity of the band at 890 cm⁻¹ may indicate the formation of MoO₂ (formation of MoO₃ particles). The bands at 665 and 945 cm⁻¹ (Fig. 2) may be ascribed to both the partial reaction of the loaded NiMo heteropoly compound with divalent Ni²⁺ ion and the formation of an AlMo compound involving surface aluminum atoms on the support (e.g., AlMo₆O₂₄H₆³⁻). The reaction of the Mo compounds loaded on alumina support has been shown to form aluminum heteropolymolybdate [26]. Accordingly, Ni²⁺ ion can exist in the salt of a new or previously loaded heteropolyanion. In the spectrum of the NiMo₆/Al-B sample, the evidence for the MoO₃ phase includes a higher band intensity at 440 cm⁻¹ and shoulders at 823 and 993 cm⁻¹. Ferdous et al. [27] observed similar changes in the FT-IR spectra of their NiMo/Al₂O₃ catalyst with 1.7 wt% boron.

2.4 UV-Vis DRS spectra

Figure 3 represents the UV-Vis DRS spectra of the samples and the initial NiMo₆ salt. In the spectra for the samples, the bands in the 200–350 nm region were characteristic of polymeric Mo–O–Mo structures exhibiting charge transfer from O²⁻ to Mo⁶⁺ with an octahedral coordination. In the low wavelength region of 200–400 nm where the contributions of both tetrahedral and octahedral Mo⁶⁺ would appear, a single broad band with a maximum at 250 nm was present. The broad shape of this charge transfer band, which resulted from the splitting of two molybdenum states, did not allow for a discrimination of the contributions from tetrahedral Mo and octahedral Mo species using the criteria in the literature [28].

Fig. 3. UV-Vis DRS spectra of different samples. (1) NiMo₆/Al-B; (2) NiMo₆/Al-Ni; (3) NiMo₆/Al-Co; (4) NiMo₆/Al; (5) NiMo₆ salt.

The appearance of the tetrahedral Mo band can be associated with the partial disorder of the heteropolyanion structure resulting from the calcination of the samples. This

band became more asymmetric at the higher frequencies with nickel and cobalt incorporation in the support, which suggested that more of the molybdenum had the octahedral coordination when these metals were first added to the support.

The band around 400 nm was observed for all of these samples, which confirmed the presence of octahedral Ni^{2+} . This band is overlapped with the strong absorption band of octahedral Mo^{6+} . This band appeared as a shoulder in the spectra of the other catalysts. In the spectrum of the initial salt, octahedral Ni^{2+} [29] was also detected at 600–700 nm. In the $\text{NiMo}_6/\text{Al-Co}$ sample, where the modified support was prepared by the prior loading of cobalt on alumina, a doublet (plateau) appeared in this region (590 and 640 nm). This plateau was not observed in the spectra of the other catalysts. Therefore, its appearance resulted from the addition of cobalt. The band was assigned to a surface spinel-like phase of CoAl_2O_4 formed during calcination with tetrahedral cobalt or with octahedral cobalt [30].

2.5 TPR spectra

The TPR profiles of the catalysts are presented in Fig. 4. TPR was carried out at 1000 °C and gave three principal peaks of hydrogen consumption (500, 680, and 920 °C). The peaks with the highest intensity were observed for the NiMo_6/Al and $\text{NiMo}_6/\text{Al-Ni}$ catalysts, and the profiles for the other two catalysts mainly differed in the high temperature region (> 500 °C). The reduction profiles corresponded to the reduction of the Anderson-type compounds [31]. The changes in the spectra were due to $\text{Mo}^{6+} \rightarrow \text{Mo}^{4+}$ and $\text{Mo}^{4+} \rightarrow \text{Mo}^0$ reduction processes. The first peak at 450–500 °C can be ascribed to the reduction of Mo^{6+} in polymeric octahedral Mo species. The other phase (Mo^{5+}) was simultaneously formed during the reduction, and was reduced to

Fig. 4. TPR profiles of the HDS catalysts. (1) NiMo_6/Al ; (2) $\text{NiMo}_6/\text{Al-Ni}$; (3) $\text{NiMo}_6/\text{Al-Co}$; (4) $\text{NiMo}_6/\text{Al-B}$.

Mo^{4+} . The peak observed at 650–700 °C resulted from the complex reduction process of these compounds. The addition of nickel to the alumina promoted the reduction of the Mo species, which then proceeded at a lower temperature (Table 2). This result indicated that in the $\text{NiMo}_6/\text{Al-Ni}$ sample, the loaded NiMo_6 interacted with the Ni-modified alumina and part of it formed another type of active site. It should be noted that the hydrogen consumption observed with $\text{NiMo}_6/\text{Al-Ni}$ began at the lowest temperature. This result is consistent with the presence of very small particles on the surface of the catalyst, which was confirmed by the presence of an amorphous phase in the XRD pattern (Fig. 1). The low intensity peak at 200 °C appearing on the $\text{NiMo}_6/\text{Al-Ni}$ profile is most likely associated with the reduction of the highly dispersed Ni^{2+} particles. The modification of alumina by cobalt only changed slightly the reduction profile for the $\text{NiMo}_6/\text{Al-Co}$ catalyst in comparison with the NiMo_6/Al sample.

The TPR profile of H_2 consumption for the $\text{NiMo}_6/\text{Al-B}$ sample was different from those of the other catalysts. The first peak appeared at a significantly higher temperature compared with the other catalysts (Table 2). The temperature (547 °C) was high enough to reduce Mo^{6+} to Mo^{4+} in the $\text{NiMo}_6/\text{Al-B}$ sample. This molybdenum state was more stable in comparison with the other samples, resulting in a significant decrease in hydrogen consumption for this sample (Table 2). In addition, the formation of other reduced species was more difficult with this sample. The formation of different Mo moieties in the presence of boron has been previously proposed [17]. One Mo moiety, MoO_3 , was observed in the IR spectrum and XRD pattern of this sample (Figs. 1 and 2). In this sample, a significant portion of the alumina surface was most likely covered by boron atoms. It has been shown that molybdenum forms a weaker bond with boron than with alumina on the surface of borated alumina [32]. Therefore, bulkier species would be formed during calcination of the sample. Thus, we can expect the formation of other species that are more difficult to reduce with this sample.

The highest reduction temperature (900 °C) observed for the samples can be ascribed to the deep reduction of the Mo

Table 2 Hydrogen consumption and ammonia desorption determined by TPD measurement

Catalyst	TPR peak maxima (°C)			H_2 consumption (mmol/g)	NH_3 desorption (mmol/g)
NiMo_6/Al	500	688	940	0.73	0.56
$\text{NiMo}_6/\text{Al-Co}$	499	712	933	0.31	0.56
$\text{NiMo}_6/\text{Al-B}$	547	—	887	0.17	0.66
$\text{NiMo}_6/\text{Al-Ni}$	460	640	920	0.56	0.63

Prior to the measurements, the catalysts were calcined for 2 h at 320 °C and then heated to 350 °C at a rate of 20°/min.

Fig. 5. NH₃-TPD profiles over the supported NiMo₆ catalysts. (1) NiMo₆/Al; (2) NiMo₆/Al-Co; (3) NiMo₆/Al-B; (4) NiMo₆/Al-Ni.

species formed during the decomposition of the loaded compound and/or to the difficult reduction of tetrahedral Mo-containing species. Quantitative data obtained from the analysis of the TPR measurements are summarized in Table 2.

2.6 NH₃-TPD results

NH₃-TPD profiles can provide information regarding the concentration and strength of the acidic sites on the catalysts. In Fig. 5, the ammonia desorption curves are depicted. There was no significant difference in the ammonia desorption curves of the catalysts. Ammonia desorption started at 60 °C, reached a maximum desorption rate at 170–180 °C and then slowly decreased, reaching a minimum at 1000 °C. The slow decrease in ammonia desorption rate with increasing temperature revealed the heterogeneity of the strength of the acidic sites. The unmodified NiMo₆/Al catalyst showed a slow and gradual decrease in ammonia de-

sorption similar to the NiMo₆/Al-Ni and NiMo₆/Al-B catalysts. In contrast, the NiMo₆/Al-Co catalyst had a second desorption peak with a maximum at 500 °C, which indicated that this catalyst possessed a slightly higher amount of strong acidic sites compared with the other catalysts. For the quantification of the acid properties in Table 2, we calculated the amount of ammonia desorbed in the range of 25–350 °C because the samples were calcined up to 350 °C prior to the measurements. The result confirmed the same amounts of acidic sites (0.56 mmol/g) on the NiMo₆/Al and NiMo₆/Al-Co catalysts and slightly higher amounts (0.63 and 0.66 mmol/g) of acidic sites on the NiMo₆/Al-Ni and NiMo₆/Al-B catalysts, respectively.

2.7 XPS results

The oxidation state of the elements in the NiMo₆ catalysts using unmodified and modified γ -alumina supports were examined using XPS for both the calcined and sulfided form. The spectra of the calcined catalysts showed Mo 3*d* and Ni 2*p* features that were characteristic of Mo⁶⁺ and Ni²⁺ in an oxide matrix. The binding energy of Mo⁶⁺ that corresponds to Mo 3*d*_{5/2} is 232.8 eV, and the binding energy of Ni²⁺ that corresponds to Ni 2*p*_{3/2} is 856.3 eV. The binding energies of the other important catalyst components are as follows: Co 2*p*_{1/2} = 797.2 eV (792.9 eV for the sulfided catalyst), Al 2*p* = 75.0 eV, B 1*s* = 192.8 eV (192.5 eV for the sulfided catalyst), S 2*p*_{3/2} = 162.0 eV, and O 1*s* = 531.5 eV. Surface atom ratios (Mo/Al, Ni/Al, Co/Al, B/Al, and S/Al) of the catalysts in the calcined and sulfided states are shown in Table 3. The Mo/Ni intensity ratio for the calcined NiMo₆/Al and NiMo₆/Al-Co catalysts was slightly lower (5.48 and 5.84, respectively) than the stoichiometric value expected for NiMo₆ heteropoly compounds. A significantly lower Mo/Ni intensity ratio (2.85) was found for the calcined NiMo₆/Al-Ni catalyst because of the modification of

Table 3 Surface atom ratios for the NiMo₆ catalysts from XPS data (photoelectron lines used in the quantification are also indicated) and the degree of metal oxide sulfidation (see Fig. 6 for more details)

Sample	Surface atomic ratio							Degree of metal oxide sulfidation (%)		
	Mo/Al	Mo/Al	Ni/Al	B/Al	Co/Al	Mo/Ni	S/Al			
	Mo 3 <i>d</i> , Al 2 <i>p</i>	Mo 3 <i>p</i> , Al 2 <i>p</i>	Ni 2 <i>p</i> , Al 2 <i>p</i>	B 1 <i>s</i> , Al 2 <i>p</i>	Co 2 <i>p</i> , Al 2 <i>p</i>	Mo 3 <i>d</i> , Ni 2 <i>p</i>	S 2 <i>p</i> , Al 2 <i>p</i>	Mo 3 <i>d</i>	Ni 2 <i>p</i> _{3/2}	Co 2 <i>p</i> _{1/2}
Calcined										
NiMo ₆ /Al	0.074	0.071	0.0135	0	0	5.48	0	0	0	—
NiMo ₆ /Al-Co	0.089	0.086	0.0153	0	0.0268	5.84	0	0	0	0
NiMo ₆ /Al-B	0.117	0.112	0.0195	0.0445	0	6.01	0	0	0	—
NiMo ₆ /Al-Ni	0.088	0.092	0.0310	0	0	2.85	0	0	0	—
Sulfided										
NiMo ₆ /Al	0.081	0.078	0.0120	0	0	6.77	0.062	31	43	—
NiMo ₆ /Al-Co	0.093	0.091	0.0178	0	0.0293	5.23	0.156	61	83	25
NiMo ₆ /Al-B	0.109	0.110	0.0144	0.0504	0	7.55	0.119	47	43	—
NiMo ₆ /Al-Ni	0.072	0.076	0.0275	0	0	2.61	0.169	71	57	—

the alumina support by nickel. After sulfidation of the catalysts, the Mo/Ni intensity ratios increased slightly for the NiMo₆/Al and NiMo₆/Al-B catalysts and decreased for the NiMo₆/Al-Co and NiMo₆/Al-Ni catalysts. The observed changes in the surface layer of the catalyst indicated decomposition of the NiMo₆ heteropoly compound and formation of bulky Mo species on the catalyst surface during sulfidation.

In the sulfided catalysts, new spectral features were observed in the Mo 3*d*, Ni 2*p*, and Co 2*p* photoelectron lines corresponding to metal sulfide phases. To illustrate these findings, the Mo 3*d* and Ni 2*p* spectra for the sulfided catalysts are shown in Fig. 6. The Mo 3*d* spectra for the sulfided NiMo₆ catalysts were decomposed into two main components (Mo⁴⁺ and Mo⁶⁺) because three components decomposition (Mo⁴⁺, Mo⁵⁺, and Mo⁶⁺) led to low level of Mo⁵⁺ for all the samples. The first component corresponded to the sulfide state with Mo 3*d*_{5/2} at 229.0 ± 0.1 eV (Mo⁴⁺), and the second one corresponded to Mo 3*d*_{3/2} at 232.6 eV (Mo⁶⁺), which represents Mo⁶⁺ in the calcined samples. As can be seen from Table 3 and Fig. 6, the degree of Mo sulfidation expressed by the ratio of Mo⁴⁺/(Mo⁴⁺ + Mo⁶⁺) was the

smallest for the catalysts prepared using unmodified alumina and boron modified alumina. The highest degree of sulfidation was found for the catalysts supported over Co- and Ni-modified alumina. In addition, the occurrence of Mo⁶⁺ in the surface layer was lower for the NiMo₆ catalysts prepared using modified alumina (Table 3).

The decomposition of the Ni 2*p*_{3/2} line for all the sulfided NiMo₆ catalysts, the Co 2*p*_{1/2} line for the NiMo₆/Al-Co catalyst, and the Mo 3*d* lines for the sulfided catalysts resulted in two components. The first component with Ni 2*p*_{3/2} (main line) at 853.4 ± 0.2 eV was attributed to Ni²⁺ in the sulfided form, and the second line at 856.4 eV was ascribed to unsulfured Ni. For cobalt, the binding energies were 792.9 eV for Co²⁺ in a sulfided form and 797.2 eV for Co²⁺ in the oxidic form (not shown here). The surface concentrations of Ni in the sulfided unmodified catalyst and NiMo₆/Al-B catalysts were lower than the concentration in the corresponding calcined catalysts (Table 3). In contrast, the surface concentration of Ni in the sulfided NiMo₆/Al-Co and NiMo₆/Al-Ni catalysts was higher than that found for their calcined counterparts. The degree of nickel sulfidation was 43% for the catalysts prepared over unmodified and B

Fig. 6. Mo 3*d* and Ni 2*p*_{3/2} photoelectron lines of NiMo catalysts on unmodified and modified supports. The spectra were decomposed into oxide and sulfide components. The degree of sulfidation was determined by the $A_{\text{Me-sulfide}}/(A_{\text{Me-sulfide}} + A_{\text{Me-oxide}})$ ratio, where Me = Mo or Ni and *A* was the component area.

modified alumina. The degree of sulfidation of nickel in the remaining catalysts, NiMo₆/Al-Co and NiMo₆/Al-Ni, was substantially higher, and were 83% and 57%, respectively.

In summary, we did not observe a significant change in the Ni/Al intensity ratio after catalyst sulfidation. Therefore, the Ni particles on the catalyst surface existed in a multi-layer structure and were partly shadowed by the MoS₂ slabs [33]. An increase in the Mo/Al ratio was observed for the oxidic and sulfided NiMo₆ catalysts supported on modified aluminas, especially for the oxidic NiMo₆/Al-B catalyst (Table 3). The formation of a borate monolayer on the alumina surface has been reported by Maity et al. [34]. Therefore, a higher proportion of the MoS₂ phase in the NiMo₆/Al-B catalyst can be expected.

2.8 HDS of BT and sulfide phase dispersion

The HDS reaction of BT was characterized by four pseudo-first order rate constants (K_1 – K_4) for the reaction scheme BT to DH, DH to BT, DH to EB, and BT to EB shown in Fig. 7. An example of the fitting the experimental data by this reaction scheme is shown in Fig. 8. Since these K_1 – K_4 rate constants do not give a measure of the overall HDS activity, the empirical pseudo-first order rate constants of BT consumption (K_{BT}) and of EB formation (K_{EB}) were calculated. An example of the fitting data by these empirical equations is also shown in Fig. 8. It is seen that the curves of BT consumption and EB formation calculated according to two above approaches are almost identical. It is the result of formation of low amounts of DH.

The HDS activities (K_{BT} and K_{EB}) of the catalysts and the sulfide phase dispersion represented by the amount of chemisorbed oxygen are shown in Table 4. Both empirical activity constants (K_{BT} and K_{EB}) possessed similar values because the formation of DH (the product of BT hydrogenation) was extremely low over all the catalysts. This is typical for the NiMo phase [35]. The modification of the support with Co, Ni, or B increased the activity of the NiMo₆ phase by 1.3–2.3 fold (based on mass-normalized activities) or 1.2–2.0 fold (based on intrinsic activities). Furthermore, the activities correlated well with the amount of chemisorbed oxygen. Clearly, the NiMo₆/Al-Ni catalyst exhibited the highest dispersion and HDS activity, which was comparable with the activity of industrial catalysts [21]. Despite the formation of DH being extremely low over all of the catalysts, there were differences in the selectivities, which were expressed as C=C hydrogenation/C–S hydrogenolysis. The selectivity for DH is shown in Fig. 9 and the values for K_1 – K_4 are summarized in Table 5. Although the relative errors for the values for K_1 – K_4 were approximately 25%, the qualitative trends were obvious. The most active NiMo₆/Al-Ni catalyst exhibited the lowest selectivity for

Fig. 7. Reaction scheme for BT HDS.

Fig. 8. Kinetic curves of the HDS of BT over NiMo₆/Al-Ni catalysts. (1) BT; (2) DH; (3) EB. solid lines calculated using the scheme of four pseudo-first order rate equations, and dashed lines calculated using an empirical pseudo-first order rate equation. a : relative composition of reaction mixture (see experimental); i : BT, EB, or DH.

Table 4 HDS activity and chemisorbed O₂

Catalyst	$K_{EB}/$ (mmol/(g·h))	$K_{BT}/$ (mmol/(g·h))	Chemisorbed O ₂ (mmol/(g·h))
NiMo ₆ /Al	171	178	12
NiMo ₆ /Al-Co	233	241	15
NiMo ₆ /Al-B	270	282	15
NiMo ₆ /Al-Ni	398	404	28

DH (Fig. 9), as revealed by the highest K_4 , which indicated direct C–S hydrogenolysis of BT to EB. The K_4 values of the other catalysts were about half of this and were quite similar. The modification of the support by Ni resulted in a significant increase in the quantity of active sites formed from the deposited NiMo₆ (dispersion measured by chemisorbed O₂) and also an increase in the quality of the active sites (the lowest selectivity for DH). XPS results also revealed that the NiMo₆/Al-Ni catalyst had the highest surface Ni concentration and the highest degree of active sulfided components.

A comparison of the catalytic activities in Tables 4 and 5 indicated a positive effect from the modification of the alumina support by additive ions (Ni, Co or B). The highest activity for HDS of BT was observed with the NiMo₆ cata-

Fig. 9. Selectivity for DH during the HDS of BT. (1) NiMo₆/Al; (2) NiMo₆/Al-Co; (3) NiMo₆/Al-B; (4) NiMo₆/Al-Ni.

Table 5 Pseudo-first order rate constants for the HDS of BT

Catalyst	Rate constant (mmol/(g·h))			
	K_1	K_2	K_3	K_4
NiMo ₆ /Al	155	15	24	5688
NiMo ₆ /Al-Co	233	5	10	5794
NiMo ₆ /Al-B	265	0	17	6188
NiMo ₆ /Al-Ni	360	0	45	13869

lyst with the alumina modified with nickel. A similar effect of support modification on the activity for the HDS of thiophene and BT was observed [21]. Furthermore, it was previously found that this preparation method led to stable and active catalyst in gas oil hydrodesulfurization performed in a pilot plant [36]. Due to the good correlation between the model HDS of BT and HDS of gas oil observed [36], the NiMo₆/Al-Ni catalyst was identified as a good candidate for further investigation in pilot plant scale HDS.

It is important to stress the higher stability of the catalysts prepared by loading Ni heteropolyoxomolybdate on alumina in comparison with Co heteropolyoxomolybdate as observed from the spectra of the catalysts (Fig. 2). This phenomenon is probably related to the different characteristics of the heteroatom. Previous adsorption studies of different Anderson heteropolyoxomolybdates suggested that nickel heteropolyoxomolybdate exhibits the lowest adsorption strength on alumina [11], which would mean that more nickel remains on the surface without forming aluminate and allows the formation of additional active sites. XPS results confirmed that the amount of surface nickel in the NiMo₆/Al-Ni catalyst significantly exceeded the amount in the other catalysts (Table 3).

The heteroatom likely plays an essential role in the counter diffusion and cationic replacement reactions. The IR spectra confirmed the formation of Al heteropolyoxo-

molybdate resulting from the reaction of the loaded NiMo₆ compound and Al atoms from the support surface:

The dissolution of alumina and the high affinity of aluminum for Anderson-type structures allows the formation of this compound in all the samples. Prior incorporation of additives (Co, Ni, B) in the alumina support helped to better preserve the heteropolyoxomolybdate structure, even for catalysts with different compositions.

Aluminum heteropolymolybdate was present in all the samples. The presence of an amorphous and highly dispersed structure in the NiMo₆/Al-Ni sample was confirmed by XRD, TPR, IR, and oxygen adsorption data. The oxygen adsorption amount was nearly twice as high for the NiMo₆/Al-Ni sample compared with the NiMo₆/Al, NiMo₆/Al-B and NiMo₆/Al-Co catalysts. It is possible that Ni, Co, and B compounds initially introduced into the alumina support interacted with the basic OH groups on the surface. The Ni²⁺ and Co²⁺ ions present on the alumina surface could interact with the loaded NiMo₆ salt by substitution of the NH₄⁺ ions. TPR measurements showed that an easily reduced phase was present in the NiMo₆/Al-Ni sample. This is likely related to a special form of nickel that is present in the catalyst, and it may be a compound similar to the Ni or Co salts of nickel heteropolyoxomolybdate. Therefore, the Ni²⁺ most likely existed in a highly dispersed form and can be reduced at low temperature, as discussed with the TPR data (Fig. 4). The absence of an inactive spinel-like phase was confirmed by the DRS spectra (Fig. 3) where bands at 620, 580, and 546 were absent [37]. With boron addition to alumina, other compounds were formed during the calcination of the NiMo₆/Al-B sample, which is in agreement with a previous work [17].

3 Conclusions

Alumina-supported NiMo hydrodesulfurization catalysts were synthesized by loading Anderson-type nickel heteropolyoxomolybdate onto alumina previously modified with nickel, cobalt, or boron. Prior nickel incorporation in the alumina to give the NiMo₆/Al-Ni catalyst (molar ratio of the total amount Ni in the catalysts was Ni/(Mo+Ni) = 0.24) resulted in an activity for HDS of BT that was nearly twice as high as the activity observed for the NiMo₆/Al, NiMo₆/Al-B, and NiMo₆/Al-Co catalysts. IR results confirmed the stability of the heteropolymolybdate structure in the calcined catalysts. A mixture of the initial and aluminum heteropolymolybdates were present in the catalysts. The highest activity observed for the Ni-modified catalyst was ascribed to the formation of the largest number of active sites.

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