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Article

Hydrodesulfurization activities of NiMo catalysts supported on mechanochemically prepared Al-Ce mixed oxides

Květa Jiráťová^{a,*}, Alla Spojakina^b, Luděk Kaluža^a, Radostina Palcheva^b, Jana Balabánová^a, Georgi Tyuliev^b

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

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

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ABSTRACT

Al₂O₃-CeO₂ supports containing 1–10 wt% Ce were prepared mechanochemically by milling aluminum and/or cerium nitrates with NH₄HCO₃. Heteropolymolybdate, (NH₄)₄NiMo₆O₂₄, was used as the precursor of the Ni and Mo to prepare NiMo₆/Al₂O₃-CeO₂ components in catalysts by impregnation method. The physicochemical properties of the catalysts were determined using chemical analysis, X-ray diffraction, temperature-programmed H₂ reduction, temperature-programmed NH₃ desorption, X-ray photoelectron spectroscopy (XPS), and the Brunauer–Emmett–Teller method. The catalyst acidity decreased with increasing Ce concentration in the support. XPS showed that the NiS/MoS ratio decreased two-fold for the Ce-modified alumina support. NiMo₆/Al₂O₃, which had the highest acidity, showed the highest activity in hydrodesulfurization of 1-benzothiophene (normalized per weight of catalyst). The concentration of surface Mo₅S₃ species (which is equal to the concentration of Mo⁵⁺) gradually decreased to zero for catalysts with Ce concentrations ≥ 10 wt%. However, the activities of all the catalysts prepared mechanochemically from Al₂O₃ and Al₂O₃-CeO₂ supports significantly exceeded that of a reference NiMo₆/Al₂O₃ catalyst prepared by impregnation method using the same precursor and with the same composition.

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1. Introduction

It is necessary to develop hydrotreatment catalysts with excellent properties because of the stringent regulations regarding the contents of sulfur compounds in transportation fuels. New and more efficient hydrodesulfurization (HDS) processes are necessary to achieve sulfur contents in petrol close to zero. A high degree of petrol HDS can be obtained using catalysts with highly dispersed active components and high levels of supported active components (Mo and W) that promote sulfidation of the loaded active phases [1].

Different approaches can be used for achieving these goals. One possibility is the use of different types of catalytic precursors

for catalyst preparation; for example, heteropoly compounds of Mo (W) with Keggin or Anderson structures can be used as active phase precursors [2–4]. In these compounds, the main components of HDS catalysts, i.e., Mo(W) and Co(Ni), are present in one molecule. It has been suggested that this increases the synergetic effect of the active components. The use of such precursors can improve the activities of HDS catalysts. Promising results have been obtained, e.g., using a CoMo/Al₂O₃ catalyst synthesized using an Anderson-type Co heteropolyoxomolybdate in the HDS of gas oil in a pilot-plant catalytic unit [5].

The choice of suitable, more effective supports is another important factor in increasing the activities of HDS catalysts [6].

* Corresponding author. Tel: +420-220390295; Fax: +420-220390111; E-mail: jiratova@icpf.cas.cz

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The support can influence the electronic and catalytic properties via electron transfer or chemical bond formation, and dispersion of the loaded components. The most frequently used support for HDS catalysts in industrial applications is γ - Al_2O_3 , but many other oxides and their mixtures have also been investigated and have shown promising results, e.g., TiO_2 , MgO , ZrO_2 , CeO_2 , TiO_2 - Al_2O_3 , SiO_2 - TiO_2 , MCM-41, and SBA-15 [7–11]. Rare-earth metal compounds have been used in catalysis for many years and their specific properties have been widely studied to enable their appropriate use. Lanthanum oxide stabilizes alumina surface properties at high temperatures [12], and retardation of sintering is connected with lanthanum aluminate formation [13]. Other rare-earth metals are also used to modify support properties. CeO_2 is one of the most studied modifiers of catalyst supports, and is believed to help to preserve the catalytic surface area, pore size distribution, and catalytic activity [14]. The addition of CeO_2 to TiO_2 retarded the transition of anatase to rutile TiO_2 crystals [15]. CeO_2 -based catalysts are particularly used in catalysts for environmental applications [12,16–18]. The presence of cerium in the support (catalyst) also improved the HDS activity of a $\text{MoS}_2/\text{Al}_2\text{O}_3$ catalyst; however, the effect was detected for only one cerium concentration [19]. The activities of NiMo/TiO_2 catalysts with ceria or alumina in the support were higher than those of catalysts prepared on simple supports. The effects of cerium on catalysts prepared over mixed oxides have not been sufficiently elucidated and there is as yet no clear explanation of their origins, e.g., synergetic effects between mixed oxides or reducing properties. It is therefore important to clarify the effects of Ce in Al-Ce mixed oxides synthesized mechanochemically [20] on the properties of NiMo catalysts for HDS reactions.

Based on literature reports of the positive effects of Ce on the physicochemical properties of Al-Ce mixed oxide supports and their increased HDS activities [19], the aim of the current study was to evaluate the effects of mechanochemically prepared γ - Al_2O_3 and Al-Ce mixed oxide supports containing various amounts of Ce on the physicochemical properties and catalytic activities of NiMo catalysts in the HDS of 1-benzothio-*phen*e (BT).

2. Experimental

2.1. Support preparation

Al_2O_3 or Al_2O_3 - CeO_2 were prepared mechanochemically from either $\text{Al}(\text{NO}_3)_3$ (Gliwice, Poland) or a mixture of $\text{Al}(\text{NO}_3)_3$ and $\text{Ce}(\text{NO}_3)_3$. $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Aldrich) was used in various proportions with NH_4HCO_3 (Lachema, Czech Republic). The procedure was described in detail in our previous paper [20]. Briefly, a mixture of $\text{Al}(\text{NO}_3)_3$ and $\text{Ce}(\text{NO}_3)_3$ was placed in a preheated oven at about 80 °C to melt. Then NH_4HCO_3 (molar ratio $\text{HCO}_3^-:\text{NO}_3^-$ 1.25:1) was added. The mixture was ground using an agate mortar and pestle mill for 1 h, dried at 60 °C for 20 h, and calcined at 500 °C for 4 h.

2.2. Catalyst preparation

A catalyst containing 12 wt% Mo and 2.0 wt% Ni was synthesized as follows. An aqueous solution of $\text{Ni}(\text{NO}_3)_2$ was added to granular Al_2O_3 or Al_2O_3 - CeO_2 supports (grain size 0.16–0.315 mm). The Ni-modified supports were dried in a vacuum evaporator at 95 °C for 1 h and an oven at 105 °C for 4 h, and calcined in air at 350 °C for 2 h at a heating rate of 1.7 °C/min. The Ni-modified supports were impregnated with an aqueous solution of $(\text{NH}_4)_4\text{Ni}(\text{OH})_6\text{Mo}_6\text{O}_{18}$ [21] in a vacuum evaporator at 70 °C. The impregnated supports were dried for 4 h at 105 °C and calcined for 2 h at 350 °C. The catalysts are denoted by the percentage weight concentration of Ce in the catalyst, e.g., $\text{Ni-Mo}_6/\text{Al-10Ce}$.

2.3. Catalyst characterization

The transition-metals contents of the catalysts were determined using atomic absorption spectroscopy. The Ce content was determined using inductively coupled plasma-atomic emission spectroscopy after dissolution of the samples in aqueous HCl.

The surface area was determined based on N_2 physisorption at –196 °C (Micromeritics ASAP 2010 instrument) after drying the samples at 105 °C and evacuating at 350 °C for approximately 2–5 h. The standard Brunauer–Emmett–Teller (BET) method was used to calculate the specific surface area, S_{BET} .

Powder X-ray diffraction (XRD) was performed using a Bruker D8 Discover diffractometer equipped with a Si-strip linear LynxEye detector and a Ge primary monochromator providing $\text{Cu } K_{\alpha 1}$ radiation ($\lambda = 1.54056 \text{ \AA}$). Data were collected in the 2θ range 3°–80°, with a step size of 0.019° and a step time of 1 s. Phase analysis was performed using DIFFRAC.EVA software (Bruker AXS GmbH, Karlsruhe, Germany; 2011).

Temperature-programmed reduction of H_2 (H_2 -TPR) was performed on the calcined samples (0.025 g) using an 10% H_2/N_2 mixture (50 mL/min) with linear temperature ramping of 20 °C/min up to 1000 °C [22]. During the TPR measurements, granular CuO (0.16–0.315 mm) was used to determine the absolute values of the amount of H_2 consumed during the reduction.

Temperature-programmed desorption of NH_3 (NH_3 -TPD) was performed at 20–1000 °C, using 0.50 g samples, with He as the carrier gas and NH_3 as the adsorbed gas. Ten doses of NH_3 were applied to the catalyst sample at 30 °C before flushing with He for 1 h and heating at a ramping rate of 20 °C/min. The mass contributions (m/z) 2- H_2 and 16- NH_3 were identified using a Balzers Omnistar mass spectrometer.

X-ray photoelectron spectroscopy (XPS) was performed using an ESCALAB-Mk II (VG Scientific) electron spectrometer with a base pressure of $\sim 5 \times 10^{-8}$ Pa. All samples were pressed into standard sample holders and inserted into the preparation chamber. After pumping to approximately 1×10^{-12} MPa, the samples were transferred to the analysis vessel for XPS characterization. Because of surface charging, calibration was performed using the C 1s line at 285.0 eV as a reference. The surface compositions were calculated from the photoelectron intensities of the O 1s, Ni 2p, Mo 3d, Ce 3d, and Al 2p lines divided by the corresponding photoelectron cross sections, taken from

Scofield [23]. Some of the sulfided samples were mounted on scotch tape to avoid differential charging, but this decreased the photoelectron intensity by a factor of two.

2.4. HDS of BT

HDS of BT was performed in the gas phase using a fixed-bed tubular-flow microreactor (i.d. 3 mm) at 360 °C and 1.6 MPa. Prior to the measurements, the catalysts were presulfided in situ in a H₂S/H₂ flow (molar ratio 1/10) at 400 °C and atmospheric pressure, with a temperature ramping rate of 10 °C/min and dwell time of 1 h. The feed composition was kept constant at 16, 200, and 1384 kPa of BT, decane, and H₂, respectively. The catalyst sample (0.02–0.05 g) was diluted with inert α -Al₂O₃ to form a bed of length 30 mm. The reaction was run at three BT feed rates, i.e., 7.7, 10.3, and 15.5 mmol/h. Steady state was reached in 30 min after each change in the feed rate. The steady state was monitored for 1 h, during which no change in the composition of the reaction mixture was observed. The reaction mixture was analyzed using a Hewlett-Packard gas chromatograph (6890 series) equipped with a capillary column (HP-5, 30 m $\times$ 0.53 mm $\times$ 1.5 μ m). Dihydrobenzothiophene (DH) and ethylbenzene (EB) were identified in the reaction products. The compositions (a_{BT} , a_{EB} , and a_{DH}) and conversions (x_{BT} , x_{EB} , and x_{DH}) are defined as $a_{BT} = (1 - x_{BT}) = n_{BT}/n^{o}_{BT}$, $a_{EB} = x_{EB} = n_{EB}/n^{o}_{BT}$, and $a_{DH} = x_{DH} = n_{DH}/n^{o}_{BT}$, where n^{o}_{BT} , n_{BT} , n_{EB} , and n_{DH} are the initial number of moles of BT, and final numbers of moles of BT, EB, and DH, respectively. The pseudo-first-order rate constant for EB formation (k_{EB}) was used as an index of HDS activity.

3. Results and discussion

3.1. Chemical analysis and porous structure

Chemical analysis showed that the initial salt synthesized in our laboratory contained 46.25 wt% Mo and 4.25 wt% Ni. The molar ratio of Ni/Mo in the initial Anderson salt was 0.16. The calculated amounts of Mo and Ni salts were used to prepare catalysts containing 12 wt% Mo and 2 wt% Ni (Ni/Mo molar ratio 0.27). The catalyst compositions are shown in Table 1. The differences among the Ni and Mo concentrations in the catalysts were small, from 1.95 to 2.03 wt% Ni and from 12.5 to 13.1 wt% Mo. The only exception was the catalyst prepared over pure CeO₂. This catalyst contained only 0.79 wt% Ni and 6.55 wt% Mo. Such low concentrations of active metals indicate

Fig. 1. XRD patterns of NiMo catalysts prepared over supports containing various amounts of Ce. (1) NiMo₆/Al₂O₃; (2) NiMo₆/Al₂O₃-1Ce; (3) NiMo₆/Al₂O₃-2Ce; (4) NiMo₆/Al₂O₃-4Ce; (5) NiMo₆/Al₂O₃-10Ce; (6) NiMo₆/CeO₂; (7) CeO₂.

that the preparation method used is not appropriate for this support, probably because of the low surface area of CeO₂.

The data in Table 1 show a gradual reduction in the catalyst surface area after loading the initial NiMo₆O₂₄ salt; for example, the alumina surface area (285 m²/g) decreased to 267 m²/g after loading the NiMo salt. This can be explained by partial blockage of micropores and small mesopores, because these contribute most to the S_{BET} . The accuracy of the surface area measurements is $\pm 10\%$, therefore the surface areas of the NiMo catalysts containing 1 and 2 wt% Ce are within the limits of accuracy. The surface areas of the catalysts containing 1 and 2 wt% Ce can therefore be considered to be identical. The meso- and micro-pore volumes decreased with increasing amount of Ce in the support. This indicates that the mesopore diameters increased. The NiMo₆/CeO₂ catalyst with pure CeO₂ as the support had the lowest surface area and mesopore and micropore volumes.

3.2. XRD

The crystal structures and phases of the NiMo catalysts calcined at 350 °C were identified using XRD. Fig. 1 shows the diffraction patterns of six samples, with Ce support contents of 0–100%. The XRD pattern of pure CeO₂ is included for comparison. The results show that all the samples had low crystallinity.

Table 1

Chemical compositions of NiMo catalysts and porous characteristics of supports and catalysts.

Sample	Catalyst						Support			
	Ce (wt%)	Ni (wt%)	Mo (wt%)	D^a (nm)	S_{BET} (m ² /g)	V_{meso} (cm ³ /g)	V_{micro} (mm ³ /g)	S_{BET} (m ² /g)	V_{meso} (cm ³ /g)	V_{micro} (mm ³ /g)
NiMo ₆ /Al ₂ O ₃	0.01	1.96	13.0	5.3	267	0.56	52	285	0.42	65
NiMo ₆ /Al ₂ O ₃ -1Ce	0.72	2.03	12.7	6.4	220	0.56	47	259	0.41	52
NiMo ₆ /Al ₂ O ₃ -2Ce	1.90	1.97	12.5	5.5	233	0.53	50	252	0.40	52
NiMo ₆ /Al ₂ O ₃ -4Ce	3.90	1.95	13.1	7.1	178	0.52	45	237	0.31	37
NiMo ₆ /Al ₂ O ₃ -10Ce	9.50	1.98	12.6	7.4	156	0.44	30	169	0.33	30
NiMo ₆ /CeO ₂	67.50	0.79	6.55	7.6	46	0.15	14	70	0.13	9

Composition of NiMo₆O₂₄: 4.25%Ni, 46.25% Mo; ^a $D = 4V_{meso}/S_{BET}$.

They show the presence of three phases, i.e., nickel aluminum oxide ($\text{Ni}_{0.941}\text{Al}_2\text{O}_{3.95}$; PDF 78-2182), nickel molybdenum oxide (NiMoO_4 ; PDF 08-0357), and aluminum oxide (Al_2O_3 ; PDF 16-0394), in the catalysts prepared over pure Al_2O_3 and Al_2O_3 with 2 wt% Ce in the catalyst. The catalyst with the smallest amount of Ce (1 wt%) was the most amorphous. For the catalysts with higher concentration of cerium ($\text{Ce} > 2$ wt%), the intensities of the CeO_2 peaks increased and those of Al_2O_3 and $\text{Ni}_{0.941}\text{Al}_2\text{O}_{3.95}$ decreased.

The calculated compositions of the main crystalline phases are shown in Table 2. The amounts of NiMo phases in the catalysts decreased with increasing amounts of cerium, probably because of high dispersion or overlapping of the NiMoO_4 and CeO_2 patterns.

3.3. TPR and TPD

TPR was performed on the catalysts in the range 25–900 °C. The results are shown in Fig. 2. Two principal H_2 consumption peaks, I at 330–560 °C and II at 560–900 °C, with maxima at around 455 and 800 °C, respectively, were observed. The changes in the H_2 signal intensities mainly arise from the reduction processes $\text{Mo}^{6+} \rightarrow \text{Mo}^{4+}$, $\text{Mo}^{4+} \rightarrow \text{Mo}^0$, and $\text{Ni}^{2+} \rightarrow \text{Ni}^0$. The first TPR peak is ascribed to the reduction of Mo^{6+} ions present as polymeric octahedral Mo species. The other Mo phase formed simultaneously during the reduction process (Mo^{5+}) can also be reduced to Mo^{4+} . The reduction profiles correspond to those reported for Anderson-type compounds [24].

The first temperature maximum, $T_{1\text{ max}}$, appeared at about 450 °C for all the catalysts containing Al_2O_3 . However, $T_{1\text{ max}}$ for the pure-ceria-supported catalyst was 358 °C. In addition to the reduction of Mo^{6+} ions, this temperature peak corresponds to the reduction of large CeO_2 particles on the catalyst surface and reduction of the formed $\text{Ce}^{3+}\text{--O--Al}$ compound [25]. This is in agreement with the previous results [26], which have shown that CeO_2 improves the reduction behavior of supported Mo compounds and stabilizes the coordination unsaturation of the reduced species.

The second intense maximum for the $\text{NiMo}_6/\text{Al}_2\text{O}_3$ catalyst, at 810 °C, is ascribed to reduction of Mo^{4+} to Mo^0 [27] and of tetrahedral monomeric molybdenum species, which interact strongly with alumina particles. Similar high-temperature peaks were observed for all the other catalysts, but at slightly lower temperatures, for example, 712 °C for the NiMo catalyst prepared over pure CeO_2 . The presence of CeO_2 in the catalyst evidently facilitates the reduction of compounds that are difficult to reduce.

Table 2

Compositions of crystalline phases in catalysts determined by XRD.

Sample	NiMoO_4 (vol%)	NiAl_2O_4 (vol%)	Al_2O_3 (vol%)	CeO_2 (vol%)
$\text{NiMo}_6/\text{Al}_2\text{O}_3$	40.1	9.6	50.4	0
$\text{NiMo}_6/\text{Al}_2\text{O}_3\text{--}1\text{Ce}$	42.6	10.9	46.4	—
$\text{NiMo}_6/\text{Al}_2\text{O}_3\text{--}2\text{Ce}$	37.6	11.4	50.9	—
$\text{NiMo}_6/\text{Al}_2\text{O}_3\text{--}4\text{Ce}$	—	—	24.2	75.8
$\text{NiMo}_6/\text{Al}_2\text{O}_3\text{--}10\text{Ce}$	—	—	28.2	71.7
$\text{NiMo}_6/\text{CeO}_2$	—	—	0	100

Fig. 2. TPR curves of NiMo catalysts. (1) $\text{NiMo}_6/\text{Al}_2\text{O}_3$; (2) $\text{NiMo}_6/\text{Al}_2\text{O}_3\text{--}1\text{Ce}$; (3) $\text{NiMo}_6/\text{Al}_2\text{O}_3\text{--}2\text{Ce}$; (4) $\text{NiMo}_6/\text{Al}_2\text{O}_3\text{--}4\text{Ce}$; (5) $\text{NiMo}_6/\text{Al}_2\text{O}_3\text{--}10\text{Ce}$; (6) $\text{NiMo}_6/\text{CeO}_2$; (7) CeO_2 .

The catalyst containing 10 wt% Ce showed a third reduction maximum at about 630 °C. This is probably related to reduction of a bulk Ce-containing phase in the catalyst, because it first appears in the sample containing 4 wt% Ce. The peaks in this temperature range could also arise from the second reduction step of the remaining octahedral Mo species [28].

The key quantitative data obtained from the TPR measurements are summarized in Table 3. The amount of H_2 consumed at 25 to 900 °C reflects the total amount of reducible components in the catalysts. However, not all these reducible compounds can be active in the HDS catalytic reaction. The amount of components that are reducible in the range 25–500 °C was therefore calculated. The amount of H_2 consumed in this temperature region (Table 3) sharply increased from 0.47 mmol/g (for the $\text{NiMo}_6/\text{Al}_2\text{O}_3$ catalyst) on introduction of small amounts of ceria (up to 2 wt%) into the catalysts. Further increasing the CeO_2 content did not change the amount of consumed H_2 ; the maximum value was 1.12 mmol H_2 /g for $\text{NiMo}_6/\text{CeO}_2$. The non-linear increase in the low-temperature region indicates that the reducibility of the catalyst does not

Table 3

Reducibilities, acidities, and HDS activities (k_{EB} at 360 °C and 1.6 MPa) of calcined NiMo catalysts.

Sample	H_2 (mmol/g)		T_{max}^a (°C)		NH_3^b (mmol/g)	k_{EB} (mmol _{EB} /g _{cat} ·h)
	25– 1000 °C	25– 500 °C	I	II		
$\text{NiMo}_6/\text{Al}_2\text{O}_3$	3.63	0.47	452	810	1.56	768
$\text{NiMo}_6/\text{Al}_2\text{O}_3\text{--}1\text{Ce}$	3.37	0.71	459	807	1.61	678
$\text{NiMo}_6/\text{Al}_2\text{O}_3\text{--}2\text{Ce}$	4.11	1.44	463	807	1.67	614
$\text{NiMo}_6/\text{Al}_2\text{O}_3\text{--}4\text{Ce}$	3.82	1.02	472	808	1.50	607
$\text{NiMo}_6/\text{Al}_2\text{O}_3\text{--}10\text{Ce}$	3.57	1.08	458	788	1.26	566
$\text{NiMo}_6/\text{CeO}_2$	1.80 ^c	1.12	358	712	0.89	15

Commercial NiMo catalyst: KF 846 Albemarle, $S_{\text{BET}} = 193 \text{ m}^2/\text{g}$, k_{EB} (360 °C) = 434 mmol_{EB}/g_{cat}·h).

^a Temperature maxima in TPR curves.

^b 25–500 °C and prior to the measurements, the catalysts were heated to 350 °C at a rate of 20 °C/min.

^c 25–650 °C.

only depend on CeO₂ addition; CeO₂ addition to Al₂O₃ at low concentrations (1–4 wt% Ce) clearly stimulates reduction of the Ni and Mo components.

The NH₃-TPD profiles in Fig. 3 show that the surfaces of all the catalysts contained acidic sites of various strengths, mainly medium and strong. The temperature maximum of NH₃ desorption shifted from 174 to 209 °C with increasing CeO₂ concentration, indicating that the strength of NH₃ bonding to the surface increased, and therefore the acid strength of the catalyst sites increased. However, the number of strongly acidic sites was smaller than that of weak ones. The total amount of acidic sites decreased with increasing Ce concentration (Table 3). The catalyst prepared on pure Al₂O₃ was the most acidic, and that on pure CeO₂ had the lowest acidity (roughly half that found of the catalyst prepared over Al₂O₃). These results show that the acidity of the mechanochemically prepared NiMo₆/Al₂O₃-CeO₂ catalysts does not change significantly up to a Ce content of 4 wt% in the catalyst. The catalyst acidity decreased with further increases in the Ce concentration. In contrast to this finding, Le Ran et al. [29] reported that the surface area and acidity increased with increasing concentration of Ce in CeO₂-Al₂O₃ supports prepared by coprecipitation. They found that the CeO₂ and Al-Ce mixed oxide acid-base properties depended on the preparation method, which influenced particle dispersion, catalyst reducibility, and catalytic activity [30]. The decrease in acidity can therefore be ascribed to segregation of CeO₂ in the catalysts with CeO₂ contents higher than 10 wt%. In contrast, a lower content of CeO₂ may be well distributed in the carrier body. The mechanochemical method of synthesis is therefore beneficial in the formation of acid-base and catalytic sites.

3.4. XPS

The oxidation states of the elements in the calcined and sulfide NiMo₆ catalysts prepared over non-modified and Ce-modified γ -Al₂O₃ supports were examined using XPS (Table 4). The Mo 3d and Ni 2p spectra of the calcined catalysts showed the presence of Mo⁶⁺ and Ni²⁺ in an oxide matrix. The Mo 3d, Ni 2p, and Ce 3d XPS spectra of the calcined Ce-modified

Fig. 3. NH₃-TPD profiles of NiMo catalysts prepared over Al-Ce mixed oxide supports. (1) NiMo₆/Al₂O₃; (2) NiMo₆/Al₂O₃-1Ce; (3) NiMo₆/Al₂O₃-2Ce; (4) NiMo₆/Al₂O₃-4Ce; (5) NiMo₆/Al₂O₃-10Ce; (6) NiMo₆/CeO₂.

γ -Al₂O₃ samples and of NiMo₆ supported on γ -Al₂O₃ and CeO₂ are shown in Fig. 4.

A binding energy corresponding to Mo 3d_{5/2} (~232.3 eV, typical of Mo⁶⁺ in oxides) was observed for the NiMo₆/Al₂O₃ catalyst. It is worth noting that the corresponding Mo 3d_{5/2} value for standard MoO₃ is higher (~233.5 eV). The binding energy of Ni²⁺ corresponding to Ni 2p_{3/2} (main peak, characteristic of Ni²⁺ in an oxide matrix) is 856.3 eV for NiMo₆/Al₂O₃ [31]. The Ce 3d spectral features indicate that Ce is mainly present in the γ -Al₂O₃-Ce supports in the Ce³⁺ oxidation state [20]. The oxidation state of Ce becomes approximately the same (3⁺) in the NiMo₆/Al-Ce catalysts.

A comparison of the Ce/(Ce + Al) ratios determined from chemical and XPS analyses (Table 5) shows that only a small amount of cerium is present on the catalyst surface. The results show that the method used for modification of the NiMo catalysts led to a low surface concentration of Ce³⁺ ions. They also show that the surface concentration of nickel, expressed as the Ni/(Al + Ce) atomic ratio, did not change up to 4 wt% Ce in the catalyst, and then increased slightly with further increases in

Table 4

Surface atomic concentrations of the calcined and sulfide NiMo₆ samples.

Calcined sample	Surface atomic concentrations (at%)					
	O 1s	Al 2p	Mo 3d _{5/2}	Ni 2p _{3/2}	S 2p _{3/2}	Ce 3d
NiMo ₆ /Al ₂ O ₃	62.55	28.73	7.29	1.44	0	0
NiMo ₆ /Al ₂ O ₃ -1Ce	61.06	31.48	5.86	1.44	0	0.16
NiMo ₆ /Al ₂ O ₃ -2Ce	62.63	28.30	7.48	1.41	0	0.18
NiMo ₆ /Al ₂ O ₃ -4Ce	60.07	34.12	4.08	1.42	0	0.31
NiMo ₆ /Al ₂ O ₃ -10Ce	61.83	26.57	9.08	2.22	0	0.30
NiMo ₆ /CeO ₂	69.65	0	11.35	2.39	0	16.60

Sulfided sample	Surface atomic concentrations (at%)										
	O 1s	Al 2p	Mo ⁴⁺	Mo ⁶⁺	MoO _x S _y	Ni sulf	Ni ox	S ²⁻	SO ₄	Ce ³⁺	Ce ⁴⁺
NiMo ₆ /Al ₂ O ₃	53.27	32.38	1.44	0.96	1.47	0.60	0.56	7.64	1.68	0	0
NiMo ₆ /Al ₂ O ₃ -1Ce	56.23	33.14	2.07	0.80	0.42	0.43	0.49	5.48	1.75	0.18	0
NiMo ₆ /Al ₂ O ₃ -2Ce	49.56	27.85	3.94	0.88	1.18	0.86	0.59	13.3	1.52	0.29	0
NiMo ₆ /Al ₂ O ₃ -4Ce	54.82	33.14	2.40	0.33	0.74	0.49	0.47	5.95	1.35	0.30	0
NiMo ₆ /Al ₂ O ₃ -10Ce	46.44	25.83	7.45	1.33	0	1.56	1.12	14.2	1.71	0.36	0
NiMo ₆ /CeO ₂	30.84	0	14.34	0.91	0	4.12	0	35.8	3.22	6.07	4.71

Fig. 4. Mo 3d, Ce 3d, and Ni 2p XPS spectra of calcined NiMo catalysts.

Table 5

Bulk and surface concentrations of Ni, Mo, and Ce in calcined and sulfided catalysts.

Sample	Concentration (mol/mol)							
	Calcined catalyst ^a			Sulfided catalysts ^b				
	Ce/(Al+Ce)	Ni/(Al+Ce)	Mo/(Al+Ce)	Ce/(Al+Ce)	Ni/(Al+Ce)	Mo/(Al+Ce)	S/(Ni+Mo)	NiS/MoS
NiMo ₆ /Al ₂ O ₃	0	0.024	0.10	0	0.050	0.253	1.85	0.21
NiMo ₆ /Al ₂ O ₃ -1Ce	0.004	0.028	0.11	0.005	0.045	0.185	1.72	0.17
NiMo ₆ /Al ₂ O ₃ -2Ce	0.012	0.029	0.11	0.006	0.049	0.262	1.99	0.17
NiMo ₆ /Al ₂ O ₃ -4Ce	0.024	0.028	0.12	0.009	0.041	0.118	1.65	0.16
NiMo ₆ /Al ₂ O ₃ -10Ce	0.068	0.034	0.13	0.011	0.082	0.338	1.39	0.21
NiMo ₆ /CeO ₂	1	0.048	0.14	1	0.144	0.683	2.01	0.29

^aChemical analysis. ^bXPS analysis.

the Ce concentration. The surface Mo concentration over the mixed Al-Ce supports, expressed as Mo/(Al + Ce), varied from 0.12 to 0.34 for the catalysts with Ce concentration less than 10 wt% and showed only random dependence on the Ce concentration. A comparison of the surface and bulk concentrations (Table 5) shows that enrichment of the surface with active metal oxide species occurred during thermal treatment of the catalysts. The surface concentration of Ni gradually increased 1.25–3-fold with increasing Ce concentration, whereas the molybdenum surface concentration increased 2.5-fold, without any dependence on the Ce concentration. Large surface exposure of Mo and Ni species in the catalysts was achieved using heteropolymolybdate NiMo₆O₂₄ as the catalyst precursor.

A systematic deconvolution of the XPS data was also performed for the sulfided catalysts. XPS was used to identify the oxidation states of Mo, Ni, and Ce and the distribution of S species on the surface. Various species (Fig. 5, Table 4) were identified on the surface. In the case of sulfided NiMo₆/Al₂O₃-Ce catalysts containing 1–4 wt% Ce, three types of Mo species, with Mo 3d_{5/2} binding energies of 228.7, 233.1, and 229.6 eV, were found; these correspond to MoS₂, MoO₃, and MoO_xS_y, respectively [32,33]. Two types of Ni were found (Fig. 5), i.e., a sulfide, NiS (Ni 2p_{3/2}, 853.9 eV), and an oxide (Ni 2p_{3/2}, 857.4 eV). All the S 2p spectra (Fig. 5) contained two S 2p doublets, the first with an S 2p_{3/2} binding energy of 161.7 eV, corresponding to S²⁻ ions in MoS₂ and/or NiS, and the second at

169.4 eV, indicating the presence of SO₄²⁻ ions in the NiMo samples. The appearance of sulfate sulfur is attributed to the oxidation of adsorbed H₂S [34] and/or oxidation during sample handling. The sulfate concentrations in the catalysts were about one-tenth of the total sulfur concentration.

Figure 5 also shows the XPS spectra of the deconvoluted Ce core electron levels for the NiMo₆/Al₂O₃-Ce samples sulfided at 400 °C. Ce 3d_{5/2} occurred as Ce³⁺ ions (binding energies 880.4 and 885.6 eV). The Ce(III) concentration varied with Ce concentration in the catalyst: the amount of Ce³⁺ ions increased with increasing Ce concentration. The quantities of Ni, Mo, Ce, and S species in the catalysts are shown in Table 5.

The Mo⁴⁺ concentration increased with increasing Ce concentration, and was the predominant species in all the catalysts. The concentration of MoO_xS_y species (equal to the concentration of Mo⁵⁺) was the highest in NiMo₆/Al₂O₃ and then gradually decreased to zero for the catalysts with Ce concentrations equal to or higher than 10 wt%. The concentration of Mo⁶⁺ did not change much with changes in the Ce concentration. About 50% of Ni species were present as sulfide in the catalysts with low Ce concentrations. The highest amount of sulfide nickel was found in the catalyst containing ~10 wt% Ce.

Deconvolution of the XPS spectra of the sulfided catalysts enabled us to estimate the degree of sulfidation of NiMo, expressed as the S/(Ni + Mo) atomic ratio; it varied from 1.39 to 2.01 (Table 5).

Fig. 5. Mo 3d, Ce 3d, and Ni 2p XPS spectra of sulfided NiMo catalysts.

3.5. HDS of BT

The catalysts were used in the conversion of BT to DH by C=C bond hydrogenation (HYD), and to EB and H₂S by C–S bond hydrogenolysis (HYG). EB and H₂S were also formed by HYG of DH. An example of quantification of the HDS activity index k_{EB} is shown in Fig. 6. The HYD/HYG selectivity is expressed as the dependence of the conversion of BT to DH (x_{DH}) on the total conversion of BT (x_{BT}), shown in Fig. 7.

Table 3 shows that the preparation of NiMo catalysts from Anderson-type heteropolyanions on mechanochemically prepared supports, i.e., γ -Al₂O₃ and cerium-modified γ -Al₂O₃, gave catalysts with activities 1.3–1.8 times higher (normalized per gram of catalyst) than those of industrial γ -Al₂O₃-supported counterparts (KF 846 Albemarle). It is also evident that pure CeO₂ is not a good support for NiMo catalysts, because NiMo₆/CeO₂ had the lowest HDS activity.

The HYD/HYG selectivity was nearly the same over the NiMo₆/Al₂O₃ and NiMo₆/Al–Ce catalysts, and was about two-fold

Fig. 6. Kinetic curves for HDS of BT over NiMo₆/Al₂O₃ catalyst at 360 °C and 1.6 MPa. Solid line is curve fitted to empirical pseudo-first-order rate equation, $a_{EB} = 1 - \exp(-k_{EB}W/F)$.

lower than that of the reference catalyst (Fig. 7). High HDS activity was therefore accompanied by low DH selectivity. Similar trends have previously been observed [31]. These results show that HYD played a minor role in the HDS of BT, because HYG accounted for 98% of the total HDS. However, increasing the CeO₂ content of the Al–Ce support decreased the k_{EB} activity, although the HYD/HYG selectivity remained the same. This suggests that the quality of the phase deposited on the mechanochemically prepared γ -Al₂O₃ was predominantly determined by interactions between Ni and Mo in the heteropolyanions and the γ -Al₂O₃ support. This results in a high synergetic effect between Ni and Mo in the phase deposited on γ -Al₂O₃.

We found a relationship between the activities of the prepared catalysts in HDS of BT and the catalyst acidity expressed as millimoles of NH₃ per gram of catalyst.

3.6. Discussion

The method used for support preparation is one of the key factors determining catalytic properties. A study of CeO₂-Al₂O₃

Fig. 7. Selectivity for DH during BT HDS at 360 °C. (1) NiMo₆/Al₂O₃ catalyst; (2) Reference industrial NiMo catalyst.

supports prepared by various methods showed that they had different chemical and physical properties, and this influenced the activities and stabilities of $\text{MoO}_3/\text{CeO}_2\text{-Al}_2\text{O}_3$ catalysts in sulfur-resistant methanation [35]. Increases in the surface areas and porosities were observed for $\text{CeO}_2\text{-Al}_2\text{O}_3$ samples synthesized by impregnation with CeO_2 [36]. In contrast, both parameters decreased when the supports were prepared mechanochemically [20].

In this study, an investigation of the HDS activities of NiMo catalysts prepared on mechanochemically obtained Al_2O_3 and $\text{Al}_2\text{O}_3\text{-CeO}_2$ supports showed that their weight-normalized activities were substantially higher than that of a reference HDS catalyst (Table 3). The surface area of the reference catalyst was lower than those of the prepared catalysts with CeO_2 contents up to 2 wt% (Table 1), but the surface-area-normalized activity was still about 1.2-fold higher. Furthermore, the activities of the investigated catalysts were higher than those of catalysts of the same compositions prepared using the same procedure [impregnation of the support with a Ni salt and then impregnation with an Anderson salt ($\text{NiMo}_6\text{O}_{24}$) solution] but on different alumina supports, as reported in our previous paper on HDS of BT [31]. The rate constants k_{EB} for BT HDS with the novel NiMo catalysts prepared over mechanochemically prepared $\text{Al}_2\text{O}_3\text{-CeO}_2$ supports were 566 to 768 mmol/(g·h), depending on the amount of CeO_2 in the catalyst, whereas that of the catalyst prepared on $\gamma\text{-Al}_2\text{O}_3$ was significantly lower ($k_{\text{EB}} = 398 \text{ mmol/(g·h)}$) [31]. The mechanochemical method used in preparation of the supports and their specific properties therefore affect the properties of the catalysts, e.g., their HDS activities.

Highly intensive homogenization (milling) of the mixture of interacting components makes mechanochemical synthesis easier. The synthesis proceeds more easily when there are acid–base interactions among the compounds, and the sorption ability of the product is increased [37,38]. As well as high dispersion of the mixed materials, mechanochemical treatment results in dense aggregate formation. The aggregate interiors can be inaccessible for surface area measurements, and for adsorption of active components. The chemical composition of the catalyst affects the porous structure and surface properties. Low concentrations of the components during mechanochemical synthesis promotes formation of dense aggregates [39]. During milling, phase evolution and heat treatment occur, resulting in changes in the product particle size and morphology. For example, Ce entities in mixed $\text{Al}_2\text{O}_3\text{-CeO}_2$ systems can be differentiated into three groups: isolated Ce ions, Ce-ion clusters, and non-dispersed CeO_2 species (CeO_2 aggregates). The relative amounts of these entities differ depending on the mixed oxide preparation method, and this affects the properties of the mixed oxide systems. The important effect of mechanochemical activation is the formation of structure imperfections. These are concentrated on the surface of the formed system and their nature and quantity determine the surface state of the product [40]. It has been suggested that higher amount of imperfections and defects increase the activity of a system.

XPS data for the mixed $\text{Al}_2\text{O}_3\text{-CeO}_2$ supports prepared mechanochemically showed that the Ce surface concentration

increased with increasing its content in the support [20]. This can affect subsequent catalyst preparation steps and the surface areas and quantities of defects in the NiMo/Al–Ce catalysts [41]. The catalyst acidity is also influenced by the presence of Ce. The catalyst acidity changed little up to 4 wt% Ce; with further increases in the Ce concentration, the catalyst acidity decreased. The XPS results suggest that Ce is located principally on the surface at low Ce concentrations (< 4 wt%) in the $\text{Al}_2\text{O}_3\text{-CeO}_2$ supports [20]. The amount of CeO_2 in the samples could decrease the numbers of surface Al–OH groups and the number of defects in the mechanochemically synthesized support. Our results (Table 3) show a linear relationship between catalytic activity in HDS of BT and catalyst acidity. The presence of Ce in the reaction system during synthesis of mixed supports leads to the disappearance of Al_2O_3 defects [41,42]. These results indicate that Ce decreases the number of acidic sites, and this decreases the activity. The concentration of NiAl_2O_4 in the samples increased with increasing Ce concentration, which also decreased the HDS activity, almost proportionally with the change in the NiAl_2O_4 concentration (except in the case of the NiMo₆/Al₂O₃-2Ce sample). However, the surface area of the NiMo₆/Al₂O₃-2Ce catalyst was nearly the same as that of NiMo₆/Al₂O₃. The decreased catalytic activity of the NiMo catalysts containing Ce could therefore be connected also with reduction of the sample surface.

The XRD patterns of the prepared samples confirmed the formation of NiMoO₄ when Ce was absent or present at low concentrations. This compound could be one of the precursors of active sites. The amount of NiMoO₄ started to decrease at about 2 wt% Ce in the catalyst. Separate bulky CeO_2 crystallites formed with further increases in the cerium concentration, which could hinder formation of the NiMoO₄ separated phase, but its presence on the surface as a highly dispersed phase cannot be excluded.

The Ni/Mo ratio in the calcined NiMo₆/Al₂O₃ catalyst (0.20), based on XPS, was close to that in the initially loaded compound (0.16). This suggests that the original Anderson compound is preserved on the catalyst surface in some form. The HDS activity of the NiMo₆/Al₂O₃ catalyst therefore depends on interactions between Ni and Mo in the heteropolyions loaded on the synthesized $\gamma\text{-Al}_2\text{O}_3$ support, resulting in high synergy between Ni and Mo in the deposited phase.

We previously suggested that higher HDS activities over NiMo catalysts were connected with higher $\text{Mo}^{5+}/\text{Mo}^{4+}$ ratios [43–45]. In this set of catalysts, the Mo^{5+} concentration was the highest in NiMo₆/Al₂O₃ and NiMo₆/Al₂O₃-2Ce. However, the S^{2-} contents on the surfaces of the other samples were higher. This could be explained by cerium sulfide formation on alumina defects. This is confirmed by the XPS results for the sample with 10 wt% Ce and for NiMo₆/CeO₂, in which large quantities of S^{2-} , but no MoO_xS_y , were observed

For all the catalysts on mechanochemically prepared supports, the sulfur contents (Table 4) increased with increasing CeO_2 content, especially when the concentration of Ce was high. Sulfidation of Ce to $\text{Ce}_2\text{O}_2\text{S}$, Ce_2S_3 , and/or Ce_2S_4 probably occurred [46].

The sporadic correlation between the catalyst characteris-

tics and HDS catalytic activities indicates that the influence of Ce on the active centers of aluminum oxide used in the mechanochemical synthesis of Al-Ce mixed oxides is random. This method of synthesizing supports is successful for Al_2O_3 but is less suitable for Al-Ce mixed oxides for HDS catalysts.

The potential of obtaining highly active NiMo catalysts using mechanochemically prepared Al_2O_3 is high. Even at 10 wt% Ce in the mixed Al_2O_3 -Ce support, the HDS activity of the NiMo catalyst exceeded that of a catalyst prepared traditionally on an industrial γ - Al_2O_3 support [31].

4. Conclusions

NiMo catalysts synthesized on mechanochemically prepared CeO_2 - Al_2O_3 supports showed higher activities in HDS of BT than a catalyst of the same composition obtained using a commercial γ - Al_2O_3 support and a reference commercial NiMo catalyst. The quantities of surface Mo, Ni, and S species in oxide and sulfide forms in the studied catalysts showed that their dependences on the amount of Ce in the catalyst were random. The phase compositions of the catalysts did not always correspond to the chemical compositions of the mechanochemically synthesized supports. The following general conclusions can be made. During mechanochemical synthesis of the supports, random disturbances of the structure probably occur, and these can affect the chemical nature of the catalyst surface. Disorder in the Al_2O_3 - CeO_2 structure of the mechanochemically prepared supports can result in inconsistent changes in the states of the active components of the NiMo catalysts with changes in the CeO_2 content. An increase in the Ce concentration in the alumina support decreases the catalyst acidity. The $\text{NiMo}_6/\text{Al}_2\text{O}_3$ catalyst showed the highest activity in HDS of BT (normalized per

weight of catalyst), which shows that the acidity and concentration of surface MoO_xS_y species (equal to the concentration of Mo^{5+}) gradually decreased to zero for catalysts with Ce concentrations ≥ 10 wt%.

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Graphical Abstract

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Hydrodesulfurization activities of NiMo catalysts supported on mechanochemically prepared Al-Ce mixed oxides

Květa Jiráťová*, Alla Spojakina, Luděk Kaluža, Radostina Palcheva, Jana Balabánová, Georgi Tyuliev
Institute of Chemical Process Fundamentals of the Academy of Sciences of the Czech Republic, Czech Republic;
Institute of Catalysis, Bulgarian Academy of Sciences, Bulgaria

NiMo catalysts synthesized over the mechanochemically prepared CeO_2 - Al_2O_3 supports (CeO_2 content less than 10 wt%) showed high activity in hydrodesulfurization (HDS) of 1-benzothiophene due to high acidity and concentration of the surface MoO_xS_y species.

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机械化学法制备的Al/Ce复合氧化物负载NiMo催化剂的加氢脱硫活性

Květa Jiráťová^a, Alla Spojakina^b, Luděk Kaluža^a, Radostina Palcheva^b,
Jana Balabánová^a, Georgi Tyuliev^b

^a捷克共和国科学院化工过程基础研究所, 布拉格, 捷克共和国

^b保加利亚科学院催化研究所, 索菲亚, 保加利亚

摘要: 将Al和/或Ce的硝酸盐与NH₄HCO₃球磨混合, 采用机械化学法制备了Al₂O₃-CeO₂载体(其中Ce含量为1–10 wt%), 再以杂多钼酸盐(NH₄)₄NiMo₆O₂₄为活性金属Ni和Mo的前驱体, 通过浸渍法制备NiMo₆/Al₂O₃-CeO₂催化剂, 并将其用于1-苯并噻吩(BT)的加氢脱硫(HDS)反应中. 运用化学分析、X射线衍射、N₂吸附-脱附法、H₂程序升温还原、NH₃程序升温脱附和X射线光电子能谱对催化剂的物化性质进行了表征. 结果表明, 催化剂的酸性随着载体中Ce含量的增加而下降. Ce修饰的Al₂O₃载体表面的NiS/MoS原子比下降了2倍. NiMo₆/Al₂O₃催化剂表现出最高的HDS活性(以单位重量催化剂计), 其酸性和表面MoO_xS_y物种的浓度(Mo⁵⁺浓度)也最高; 当催化剂中Ce含量逐渐增加到10 wt%以上时, 其活性逐渐将为0. 与浸渍法制得的参比催化剂相比, 前驱体和催化剂组成相同的情况下, 采用机械化学法制得的所有催化剂活性明显提高.

关键词: 镍; 钼; 氧化铝; 氧化铈; Anderson型杂多钼酸盐; 1-苯并噻吩; 加氢脱硫; 机械化学法

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*通讯联系人. 电话: +420-220390295; 传真: +420-220390111; 电子信箱: jiratova@icpf.cas.cz

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