# HYDRODESULFURIZATION OF DIFFERENT FEEDS ON $CoMo/Al_2O_3$ CATALYST PREPARED USING COBALT HETEROPOLYOXOMOLYBDATE

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$CoMo/Al_2O_3$ catalyst prepared by impregnation of alumina support with cobalt heteropolyoxomolybdate was tested in hydrodesulfurization (HDS) of thiophene, 1-benzothiophene, or light gas oil under various reaction conditions and reactor arrangements. Its physicochemical properties are also examined. The obtained data are compared with those of two industrial HDS catalysts.

**Keywords**: $CoMo/Al_2O_3$; Co heteropolyoxomolybdate; HDS.

Stringent environmental legislation makes the production of low-sulfur fuels a very important problem. Improvement of the catalysts currently used in the industrial HDS units is one of the possibilities how to solve the problem. $Co(Ni)Mo(W)/Al_2O_3$ catalytic systems have been used for many years as catalysts in hydrotreatment of various oil fractions. Many scientists have studied the synthesis of catalysts active in the processes and shown a synergetic effect of the active components[1,2]. Various relationships between catalytic activity and the total component content and their ratio were also observed[2]. The optimum activity of the conventional CoMo catalysts has been found at the Co/(Co+Mo) molar ratio 0.25–0.4. The optimum ratio depends mainly on the carrier properties. Although many supports have been studied in literature ($TiO_2$, $Al_2O_3$–$TiO_2$, $SiO_2$, MgO and others), the most commonly used support for the hydrotreating catalyst is $\gamma$-$Al_2O_3$. One of

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the important factors affecting catalytic activity is interaction between support and the active components.

Due to their high activity in various industrial processes, Mo(W) heteropoly compounds (HPC) have become very attractive in heterogeneous catalysis[3]. The heteropoly compounds are especially interesting for preparation of hydrotreatment catalysts because they contain both basic and promoting elements (heteropolyanion and countercation) in a single compound of defined structure and so they provide an intimate contact of both elements. Earlier we elucidated[4] that both Al and Co heteropolymolybdates impregnated or directly synthesized on the alumina surface can play, along with other molybdenum compounds, an essential role as precursors in formation of active sites in thiophene hydrogenolysis. We also revealed that water-soluble heteropolymolybdates are present on the surface after calcination at 500 °C. Promising hydrotreating activity of catalysts prepared using the heteropoly compounds as active phase precursors has been reported in some other papers[5–12]. These catalysts are potentially interesting for industrial applications. The study of HPC and their salts loaded on the appropriate supports can be used for modeling of HDS catalysts to gain an additional knowledge about effect of promoter and support on the catalyst phase composition and its HDS activity.

The aim of this contribution was to prepare a $CoMo/Al_2O_3$ catalyst by impregnation of an industrial alumina support with cobalt heteropolyoxomolybdate, to examine its physicochemical properties and catalytic activity in HDS reactions with different reactants (thiophene, 1-benzothiophene, light gas oil), reaction conditions and reactors. Two industrial HDS catalysts were examined in order to get objective information on the activity of the laboratory catalyst in relation to those of the industrial catalysts.

## EXPERIMENTAL

### Catalyst Preparation

The catalyst has been prepared by impregnation of alumina spheres ($S_{BET}$ = 200 $m^2/g$) with an aqueous solution of cobalt heteropolyoxomolybdate. The compound $(NH_4)_3Co(OH)_6$-$Mo_6O_{18}$ was synthesized according to literature[13]. The support was preliminarily loaded with an amount of cobalt using an aqueous solution of $Co(NO_3)_2$ in order to increase the Co/Mo molar ratio in the catalyst to the required value. The support beads were treated with an aqueous solution of the salt in a vacuum evaporator. The moist catalyst precursor was dried at 105 °C for 4 h and calcined in air at 350 °C, the heating rate being 1.7 °C $min^{-1}$. The maximum temperature was maintained for 2 h. The prepared $Co/Al_2O_3$ was loaded with an aqueous solution of Co heteropolyoxomolybdate in a vacuum evaporator. The catalyst (CZA3) was dried at 105 °C and calcined at 350 °C for 2 h.

### Catalyst Characterization

The Co heteropolymolydate catalyst (CZA3) and two industrial catalysts, denoted as A and B, were characterized by various physicochemical methods.

The transition metal content in the catalysts was determined by AAS. The surface area and distribution of pores were determined by measuring the adsorption-desorption isotherms of nitrogen at –195 °C. The porous structure of the catalysts or support was characterized using a Micromeritics ASAP 2010 after drying the samples at 105 °C and evacuation at 350 °C to $10^{-5}$ Pa (usually 2–5 h). The data were treated by the standard BET method to calculate surface area $S_{BET}$. The volume of pores $V$(p) was calculated from the amount of $N_2$ adsorbed at $P/P_o$ = 0.98 and the volume of micropores $V_{micro}$ determined by the t-plot method and evaluated according to Schneider[14].

IR spectrum (400–1200 $cm^{-1}$) was recorded at room temperature on a Bruker IFS-25 Fourier transform IR spectrometer. The catalysts were pressed with KBr in the ratio 1:150. Alumina absorption in the 400–1200 $cm^{-1}$ range was compensated by subtraction of a normalized spectrum of an equivalent amount of support from the spectra of the catalysts.

Temperature-programmed reduction (TPR) measurements were carried out in an apparatus described earlier[15]. A hydrogen/nitrogen mixture (10 mole% $H_2$) was used to reduce catalysts at a flow rate of 17 $cm^3$ $min^{-1}$. The temperature was raised linearly at a rate of 20 °C $min^{-1}$ up to 850 °C.

### Catalytic Activity and Selectivity

*HDS of thiophene.* Hydrodesulfurization of thiophene was performed in a continuous flow reactor at 350 °C and atmospheric pressure. Each experiment was made with 0.2–0.4 mm particles of a fresh catalyst (100 mg). The catalyst was standardized by in-situ heating (1 h) in argon at 350 °C and activated by sulfidation with a $H_2S + H_2$ (10% $H_2S$) at 350 °C for 1 h and flow rate 40 $cm^3$ $min^{-1}$. After the activation procedure, the catalyst was flushed (30 min) with argon at the same temperature, and then, feeding the reaction mixture (6 mole % of thiophene in hydrogen), the thiophene conversion was started at 1 and 3.2 $h^{-1}$. The catalyst activity was measured for 5 h and expressed as the thiophene conversion to $C_4$ hydrocarbons.

*HDS of 1-benzothiophene.* The catalysts were crushed and sieved to particle size 0.2–0.32 mm. The catalysts in amounts 20 mg were diluted with 180 mg of $\alpha$-$Al_2O_3$ and placed into a tubular flow microreactor of the inner diameter 3 mm. The catalyst bed was in-situ presulfidized in the flow of $H_2S/H_2$ (1:10) with temperature ramp 10 °C $min^{-1}$ to 400 °C and dwell 1 h. The starting reaction mixture consisted of 16, 200, and 1384 kPa of 1-benzothiophene, decane, and hydrogen, respectively. The 1-benzothiophene (BT), dihydrobenzothiophene (DH) and ethylbenzene (EB) in the products of the reaction at 360 °C at three feed rates of 1-benzothiophene (7.7, 10.3, and 15.5 mmol $h^{-1}$) were analyzed using a gas chromatograph HP 6890 Series. The steady state was reached 20 min after each change of the reaction conditions; deactivation of the catalysts was not observed. The relative compositions $a_{BT}$, $a_{EB}$ and $a_{DH}$ and conversions $x_{BT}$, $x_{EB}$, and $x_{DH}$ were defined as $a_{BT} = (1 - x_{BT}) = n_{BT}/n^o_{BT}$, $a_{EB} = x_{EB} = n_{EB}/n^o_{BT}$, $a_{DH} = x_{DH} = n_{DH}/n^o_{BT}$, where $n^o_{BT}$ and $n_{BT}$, $n_{EB}$, $n_{DH}$ are the initial number of moles of BT and final number of moles of BT, EB, DH, respectively.

*HDS of gas oil in pilot-plant catalytic unit.* Examination of the catalytic activity was carried out in a pilot-plant HDS unit working at 3 MPa. The catalyst bed consisted of 100 ml of a catalyst in its original form diluted with an equal volume of SiC particles (1–1.5 mm).

The reaction was carried out at 360 °C and at total pressure 3 MPa. The raw material used in the experiments (light gas oil) was prepared from Russian crude oil (known as a Russian export blend) in the refinery Litvínov (Czech Republic). Its characteristics are given in Table I. The commercial catalysts were in-situ sulfided following the procedures given by their manufacturers. The CZA3 catalyst was sulfided in situ in the following manner: hydrogen (50 $dm^3$ $h^{-1}$) and hydrogen sulfide (15 g $H_2S$ $m^{-3}$) were fed onto the catalyst with simultaneous addition of light gas oil containing 1% DMDS (dimethyl disulfide) in the amount of 200 g $h^{-1}$. Temperature of the catalyst layer was increased from ca. 20 up to 360 °C with temperature ramp 15 °C $h^{-1}$. The catalysts were tested at space velocity 1.0 kg $dm_{cat}^{-3}$ $h^{-1}$ and hydrogen pressure 3.0 MPa. After achieving the steady state, an average sample of reaction products was collected and then analyzed for sulfur using the ASTMD 3120 Oxidative microcoulometric method (Dohrman ECS1200).

TABLE I
Distillation curve and properties of the light gas oil used in the pilot-plant unit

| Distillation curve | | | Properties | |
|---|---|---|---|---|
| | ASTM D86 | SYMDIST | | |
| Portion[a,b] | °C | °C | Density (15 °C, kg $m^{-3}$ | 855 |
| 0 | 228.3 | 150 | Refraction index (20 °C) | 1.4749 |
| 3 | 247.4 | 202.5 | Sulfur, mg $kg^{-1}$ | 8710 |
| 5 | 253.6 | 219 | Nitrogen, mg $kg^{-1}$ | 120.3 |
| 10 | 267 | 240 | Color – ASTM 1500 | 0.3 |
| 30 | 279.2 | 274 | | |
| 50 | 293.1 | 299 | Composition[c], wt.% | |
| 70 | 308.9 | 322 | Saturated | 67.1 |
| 90 | 332.9 | 355.5 | Monoaromatics | 20.5 |
| 95 | 343.2 | 369 | Diaromatics | 11.18 |
| 97 | 349.5 | 376.5 | Triaromatics | 0.6 |
| 100 | 356.3 | 401 | | |
| Fractions | | wt.% | | |
| >300 °C | | 49.5 | | |
| >320 °C | | 32.5 | | |
| >330 °C | | 24.5 | | |
| >360 °C | | 17.9 | | |

[a] Portion values in vol.%. [b] Portion values in wt.%. [c] Determined by HPLC.

## RESULTS

### *Characterization of the Catalysts*

Physicochemical properties of all catalysts were investigated before their testing in order to understand possible differences in their catalytic activity.

### Chemical Analysis and Porous Structure of the Catalysts

Chemical analysis of all catalysts (Table II) showed that the CZA3 catalyst contains approximately 50% of the components present in both examined industrial catalysts. The Co/(Co+Mo) mole ratio in these catalysts (0.20–0.22) differ only a little.

TABLE II
Physicochemical properties of the examined catalysts

| Property | CZA3[a] | A | B | CZA3[b] |
|---|---|---|---|---|
| Shape | beads | extrudates | trilobe[c] | beads |
| Diameter, mm | 2.5 | 1.5 | 1.3 | 2.5 |
| Mo, wt.% | 7.37 | 13.74 | 11.85 | n.d. |
| Co, wt.% | 1.13 | 2.43 | 2.05 | n.d. |
| (Co+Mo), mmol $g^{-1}$ | 0.96 | 1.84 | 1.58 | n.d. |
| Co/(Co+Mo), mole/mole | 0.20 | 0.22 | 0.22 | n.d. |
| Bed density, g $dm^{-3}$ | 961[d] | 800 | 990 | n.d. |
| $S_{BET}$, $m^2$ $g^{-1}$ | 166.3 | 132.9 | 13.0 | 188.7 |
| $C_{BET}$ | 152.7 | 64.1 | 0.99 | 344.7 |
| $S_{meso}$, $m^2$ $g^{-1}$ | 160.7 | 128.3 | 12.9 | 18 |
| $V_{micro}$, $mm^3$ $g^{-1}$ | 4.5 | 3.9 | 0.1 | 18 |
| $C_{modif}$ | 106.2 | 50 | 20.1 | 92.3 |
| $V^e$, $cm^3$ $g^{-1}$ | 0.37 | 0.34 | 0.04 | 0.48 |
| Pore diameter ($4V/S_{BET}$), nm | 8.2 | 9.0 | ~4 | 9.0 |

[a] Fresh catalyst. [b] After pilot-plant testing. [c] Trilobe is an extrudate comprising three tightly connected small cyliders. [d] Bed intensity of the carrier. [e] Total pore volume determined from adsorption of $N_2$.

The bed density of the examined catalysts differs to large extent (see Table II). The lowest one (716 g $dm^{-3}$) was found for catalyst A, while the highest (990 g $dm^{-3}$) for catalyst B. The bed density of CZA3 approaches the value of catalyst B.

Characteristic values of the catalyst porous structure can also be seen in Table II. The surface area of the CZA3 catalyst is by 20% higher than that of catalyst A. Different $C_{BET}$ constants in the BET equation for the catalysts indicate differences in sorption properties of their surfaces. All catalysts show negligible volume of micropores $V_{micro}$ and, from that reason, surface of mesopores equals to BET surface area. Modified adsorption constants $C_{modif}$ characterizing sorption properties of the catalyst surfaces confirm variety in the properties of the examined catalysts. Pore volumes and average pore diameter of the CZA3 and A catalysts are approximately the same. Contrary to the properties of previously discussed catalysts, examination of the industrial B catalyst did not give any reasonable information about its porous structure. Though the catalyst was treated prior to the measurement with an extraction agent (cyclohexane) to remove a compound used for catalyst sulfidation, the found surface area was substantially lower than those of other two catalysts, reaching only the value 14 $m^2$ $g^{-1}$. Unexpectedly low is also its pore volume. Adsorption–desorption isotherms of nitrogen obtained over the catalyst confirm incomplete removal of the sulfidation compound in extraction and the following standard catalyst pretreatment (Fig. 1). For that reason, the surface area and pore volume of catalyst B do not reflect its real porous structure.

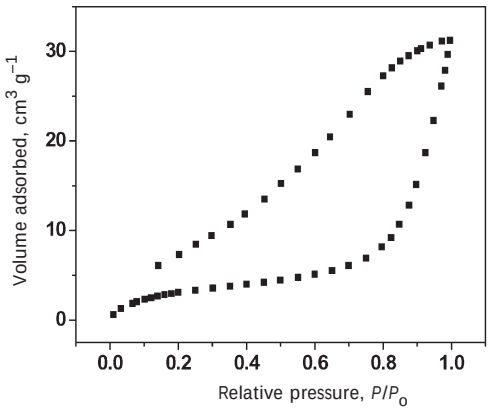


FIG. 1
Adsorption–desorption nitrogen isotherms of the industrial catalyst B

## IR Spectra

IR spectra of the CZA3 catalyst prepared from cobalt heteropolyoxometalate and of two industrial catalysts are summarized in Fig. 2. The spectrum of the CZA3 catalyst shows the bands at 445, 668, 890 $cm^{-1}$ and low-intensity bands at 945 and 990 $cm^{-1}$. The band at 890 $cm^{-1}$ characterizes vibration of tetrahedral $Mo{=}O_t$ bonds of highly polymerized molybdenum compounds[16]. The bands at 668 and 445 $cm^{-1}$ are characteristic of the Mo–O–Mo bridges. These bands along with the bands in the high-frequency region (880–950 $cm^{-1}$) indicate the formation of a new structure or a new surface compound, analogous to aluminium heteropolyoxomolybdate[17,18]. In the ~668 $cm^{-1}$ region, the bands of original Co heteropolyoxomolybdate could be overlapped with the bands of Al heteropolyoxomolybdate formed as a result of the initial compound with the support.

The IR spectra of the industrial catalysts substantially differ from that of CZA3. In the spectra of both industrial catalysts, large plateaus with pronounced peaks at 560, 650–660, and ~800 $cm^{-1}$ can be observed. The spectrum of the B catalyst resembles that of CZA3: the bands at 890 and ca. 650 $cm^{-1}$ appear on the base of the plateau and, therefore, we can assume a higher number of Mo–O–Mo sites compared with tetrahedral $Mo{=}O_t$ in both catalysts. On the other hand, in the IR spectrum of the A catalyst, tetrahedral $Mo{=}O_t$ sites likely prevail as a large shoulder can be observed at ca. 890 $cm^{-1}$. In the spectra of the industrial catalysts, the bands in the

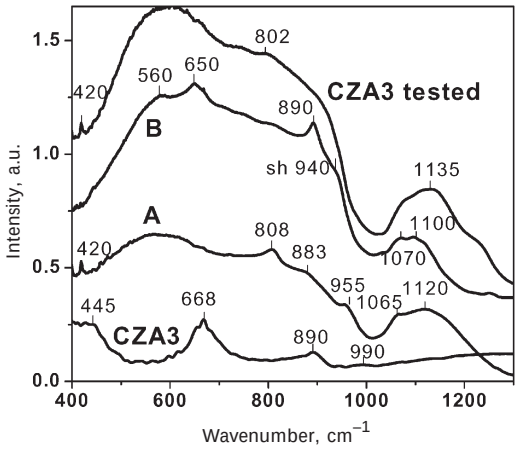


FIG. 2
IR spectra of the examined catalysts

1000–1200 $cm^{-1}$ region missing in the spectrum of the fresh CZA3 catalyst can be observed. Their presence could indicate the occurrence of molybdates and/or phosphates in the catalysts.

## Temperature-Programmed Reduction of the Studied Catalysts

Reduction patterns of all catalysts are shown in Fig. 3 and the consumptions of hydrogen necessary for reduction of different reducible phases (up to 860 °C) are presented in Table III. Resolution of the TPR spectra was made with an Origin 7.5 Peak fitting module.

The TPR pattern of the synthesized CZA3 catalyst reveals two strong peaks at $T_{max}$ = 440 and 738 °C. The same peaks, only more intensive, have been revealed in the dried catalyst. Therefore, we can judge that similar Mo species are present in both dry and calcined catalyst. This fact is in accord with our previous results[4] where water-soluble polymolybdate species were confirmed after calcination of similar CoMo catalyst by Raman spectroscopy. In the profile of the A catalyst three peaks can be identified (at 317, 464 and >800 °C), and in the TPR pattern of the catalyst B a very strong low-temperature peak (at 347 °C) together with the shoulders at 462 and 605 °C. The form of the peaks appearing in both reduction patterns of both catalysts indicate, very likely, the occurrence of the same phase but of different dispersion and amount.

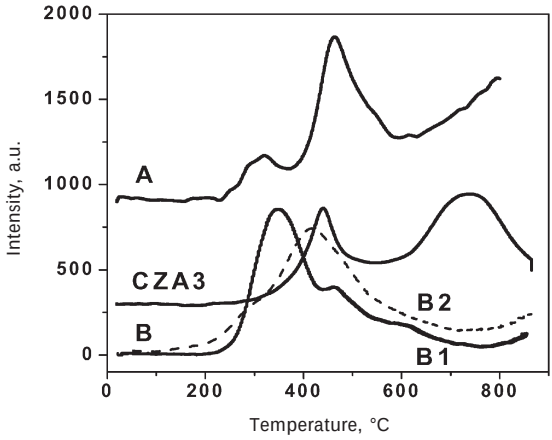


FIG. 3
TPR patterns of the examined CZA3, A and B catalysts (B1 – after extraction with cyclohexane and dryed at 105 °C, B2 – after calcination in helium up to 400 °C)

TABLE III

Experimental values for the consumed hydrogen (in mmol $H_2$ $mmol_{(Mo+Co)}^{-1}$) determined by resolution of the TPR patterns of the examined catalysts, calculated per 1 mmol of active component

| Catalyst | mmol $H_2$ $mmol_{(Mo+Co)}^{-1}/T_{max}$, °C | | | | | mmol $H_2$ $mmol_{(Mo+Co)}^{-1}$ | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | | <487 °C | <600 °C | <865 °C |
| CZA3 | 0 | 0 | $0.688/_{436}$ | $0.188/_{541}$ | $1.343/_{739}$ | 0.69 | 0.99 | 2.22 |
| A | $0.165/_{310}$ | 0 | $1.119/_{462}$ | $0.184/_{533}$ | $1.230/_{820}$ | 1.29 | 1.62 | 2.71 |
| B[a] | $1.669/_{348}$ | 0 | $0.802/_{472}$ | $0.396/_{583}$ | $0.254/_{851}$ | 2.47 | 2.66 | 3.12 |
| B[b] | $0.177/_{302}$ | $1.278/_{409}$ | $0.891/_{480}$ | $0.251/_{696}$ | $0.226/_{851}$ | 0.48 | 2.37 | 2.85 |

[a] After extraction of the catalyst with cyclohexane and drying at 105 °C. [b] After calcination of the catalyst in He up to 400 °C.

The low-temperature peak appearing in the region 440–480 °C can be ascribed[19] to partial reduction of well-dispersed polymeric octahedral Mo species, i.e. $Mo^{6+}$ to $Mo^{4+}$. The high-temperature peak occurring at temperatures higher than 700 °C (739 °C for CZA3 catalyst and 820–851 °C for catalysts A and B) can be attributed to the second step in reduction of the polymeric octahedral Mo species ($Mo^{4+}$ to $Mo^{0}$). Very high temperature of the high-temperature peaks indicates reduction of the tetrahedral $Mo^{6+}$ species that are in a strong interaction with the support[20].

As the hydrogen consumption is concerned, the highest amount of hydrogen consumed during TPR up to 600 °C (more than 50% of total amount) is observed with catalyst B (see Table III). It was found earlier that the reduction temperature and the peak width tend to decrease with decreasing size of reducible particles[21]. That is why a highly dispersed phase (easily reducible at 347 °C) can be expected in the non-calcined industrial B catalyst. The species, which are not bonded very strongly to the support, are reduced at higher temperatures (472 and 583 °C). After calcination of catalyst B at 400 °C the reducible sites become more heterogeneous and the amount of highly dispersed, easily reducible sites decreases (see Table III).

Substantially different situation in the process of reduction of catalyst A can be observed from its TPR pattern. It shows the most heterogeneous mixture of molybdenum species of all examined catalysts with prevailing sites reducible at higher temperatures.

The catalyst CZA3 contains a lower amount of the easily reducible phase than both A and B catalysts. The finding is understandable as the amount of active components in this catalyst is lower than that in the other. Nevertheless, the $T_{max}$ of the low-temperature peak indicating highly dispersed, easily reducible molybdenum sites is approaching the $T_{max}$ of catalyst B.

### *Catalytic Activity*

An integral part of every development of a catalyst is testing of its activity. Various model feed reactions for testing HDS catalysts can be found in literature: thiophene, 1-benzothiophene and dibenzothiophene HDS are most often used. The use of thiophene is the simplest as the tests can be made under atmospheric pressure. Some objections to this model reaction exist, the low reaction pressure and a very low boiling point of the reactant being the most important. The properties of 1-benzothiophene, compound with boiling point higher than thiophene, are closer to real HDS substrates. Moreover, it can give additional information on the selectivity of active sites of the catalyst. The same applies to dibenzothiophene.

The activity tests of the HDS catalysts in laboratory, which use individual chemical compounds as reactants, are more rapid and cheaper. However, the reaction conditions are far away from the industrial reactions conditions and that is why the most important source of information on the HDS catalyst still remains the test with a real raw material performed in a pilot-plant unit. For the sake of complex characterization of the examined catalysts, two model sulfur compounds (thiophene, 1-benzothiophene) and the real raw material (light gas oil) were chosen in this study. The test reactions were performed in three arrangements: in two laboratory reactors working under either atmospheric or increased pressure, and in a pilot-plant unit simulating industrial HDS conditions.

## Hydrodesulfurization of Thiophene

Hydrodesulfurization of thiophene (Th) over the examined catalysts was performed in a laboratory reactor filled with catalyst grains and working at space velocity 1 $g_{Th}\ g_{cat}^{-1}\ h^{-1}$ and atmospheric pressure. The obtained thiophene conversions are summarized in Table IV. When the catalyst activity is related to the weight of the catalyst, its order is as follows: At high reaction temperature (350 °C), conversions of thiophene hydrodesulfurization are comparable for both CZA3 and industrial B catalysts. When reaction temperature decreased to 300 °C, the order of catalyst activity changed as follows: catalyst B > CZA3 = catalyst A. Catalyst B evidently preserves its high activity at low reaction temperature (300 °C) and, therefore, it can work almost with the same parameters as those obtained at high reaction temperatures. On the other hand, thiophene conversion over the CZA3 cat-

TABLE IV
Thiophene conversions (in %) observed over the examined catalysts

| $T$, °C | $F/W$, $g_{Th}\ h^{-1}\ g_{cat}^{-1}$ | Thiophene conversion, % | | |
|---|---|---|---|---|
| | | CZA3 | catalyst A | catalyst B |
| 350 | 3.2 | 40.0 | 25.0 | 49.0 |
| | 1.0 | 60.0 | 45.0 | 63.0 |
| 300 | 3.2 | 20.0 | 20.0 | 42.0 |
| | 1.0 | 36.0 | 37.0 | 60.0 |

alyst decreased with decreasing reaction temperature. Nevertheless, the activity of the CZA3 catalyst determined at 300 °C was comparable with that of the industrial catalyst A.

## Hydrodesulfurization of 1-Benzothiophene

1-Benzothiophene (BT) hydrodesulfurization proceeds in the following way. Dihydrobenzothiophene (DH) is formed by hydrogenation reaction (HYD), ethylbenzene (EB) is formed by hydrogenolysis (HYG) of both mentioned reaction components. It is believed[22] that changes in relative selectivity (HYG/HYD) reflect changes in quality of catalyst active sites.

An example of the dependence of the reaction mixture composition on space time in HDS of 1-benzothiophene (BT) is shown in Fig. 3. The HDS process was described with a scheme of four parallel consecutive reactions of pseudo-first order: hydrogenation of BT to DH, dehydrogenation of DH to BT, and hydrogenolysis of both BT and DH to EB. Because none of them represented a proper measure of overall HDS activity, a formal pseudo-first order rate constant of EB formation was used as an activity measure. An example of fitting of the four rate constants and formal EB rate constants is also given in Fig. 4.

It was found that the normalized (per g) HDS activity was the highest for catalyst A, followed by catalyst B and the lowest value was found for CZA3. However, because of about 50% content of Co and Mo in CZA3 compared

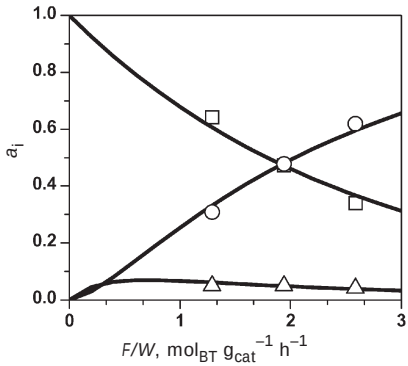


FIG. 4

Reaction mixture compositions at various space times $W/F$ during HDS of 1-benzothiophene over CZA3. □ 1-benzothiophene $a_{BT}$, △ dihydrobenzothiophene $a_{DH}$, ○ ethylbenzene $a_{EB}$; solid lines: four-rate-constant scheme fitting, dashed line: first-order-rate fitting of EB conversion

with the industrial catalysts, the catalyst activity normalized per mol of (Co+Mo) showed the order: A > CZA3 > B. Quantitative comparison is given below in Discussion and in Table V.

TABLE V
HDS of the light gas oil in a pilot-plant unit at 360 °C, 3 MPa and $F/W$ = 1.0 kg $dm_{cat}^{-3}$ $h^{-1}$. Initial sulfur content in the gas oil: 8710 mg $kg^{-1}$

| Catalyst | CZA3 – beads | | | A – extrudates | B – trilobe[a] | |
|---|---|---|---|---|---|---|
| Test | 1 | 2[b] | 1[c] | 1 | 1 | 2[d] |
| Density, kg $m^{-3}$ | 844.0 | 844.1 | 843.7 | 843.1 | 842.7 | 843.3 |
| Sulfur, mg $kg^{-1}$ | 62.4 | 61.5 | 25.9 | 7.1 | 15.2 | 23.1[d] |
| HDS, % | 99.28 | 99.28 | 99.70 | 99.92 | 99.83 | 99.74 |
| Time[e], h | 17 | 6 | 17 | 48 | 24 | 48 |

[a] Three small extrudates tightly connected together. [b] Repeated test. [c] Reaction temperature 370 °C. [d] The date obtained after repeating the initial reaction conditions (after ca. 500 h). [e] The time of sample withdrawing.

The ratio $x_{EB}/x_{DHBT}$ at 50% conversion of BT was calculated and used as the (HYG/HYD) selectivity index in order to analyze catalyst selectivity quantitatively. The obtained selectivity index was 9.7, 9.0 and 10.3 for the catalysts A, CZA3 and B, respectively. It was concluded that the selectivity is quite similar and hence, the quality of the active sites in the catalysts studied do not significantly differ. Moreover, the selectivities found here were practically the same as those found earlier for typical CoMo catalysts. For example, the catalyst prepared by successive deposition[23] (Mo followed by Co) over $\gamma$-$Al_2O_3$ by impregnation with excess of an aqueous solution of $(NH_4)_6Mo_7O_{24}$ and $Co(NO_3)_2$ and the industrial CoMo catalyst KF 756 exhibited[24] the selectivity index 9.0 and 8.6, respectively. With respect to HDS of 1-benzothiophene, it could be concluded that the deposition of cobalt heteropolyoxomolybdate leads to practically the same dispersion (the same number of active sites in the catalyst) and the same quality as in the industrial catalysts studied for comparison.

## Hydrodesulfurization of Gas Oil

The results obtained with HDS of the real feed in the pilot-plant unit under industrial conditions are given in Table VI. At the reaction temperature

360 °C, the activity of the catalyst B is the highest. The conversion of gas oil is comparably high for all catalysts after 500 h.

The results obtained in the pilot-plant catalytic unit should not reflect the potential maximum activity of the CZA3 catalyst, since not all the catalysts examined have the same particle diameter. The diameter of the CZA3 catalyst beads is substantially higher than the equivalent diameter of other industrial catalysts. It is can be assumed that a decrease in the diameter of CZA3 particles would lead to an increase in catalyst activity.

TABLE VI

Relative catalyst activities based on the rate constants $k$ of the pseudo-first order reaction (calculated from the equation $k = -\ln(1 - \alpha/100)/P\,F/W$), rate constant of CZA3 being chosen as a standard

| Catalyst | CZA3 | A | B |
|---|---|---|---|
| Thiophene[a] | 1 | 0.34 | 0.66 |
| Thiophene[b] | 1 | 0.54 | 1.25 |
| Benzothiophene[a] | 1 | 1.29 | 0.79 |
| Light gas oil[a] | 1 | 0.91 | 0.76 |

[a] Reaction temperature 350 °C. [b] Reaction temperature 300 °C.

## DISCUSSION

In order to determine specific activity of the catalytic components present in the examined catalysts, the reaction rate constants $k$ of the pseudo-first order were calculated according to the equation $k = -\ln(1 - \alpha/100)/P\,F/W$, where $k$ means the amount in g of reactant converted per hour per gram of catalyst, $\alpha$ is conversion, $F$ is the feed rate (g of reactant $h^{-1}$) and $W$ the amount of catalyst (in g). The calculated values were related to the unit amount of cobalt and molybdenum (in moles); they are denoted as $\kappa$ and their dimension is $g_{reactant}\ h^{-1}\ MPa^{-1}\ mol_{(Co+Mo)}^{-1}$. Relative values of activities were calculated from the obtained rate constants $\kappa$ taking the values for CZA3 catalysts as standard values (see Table V). The order of the catalyst activities in thiophene conversion in this way calculated slightly changes compared with those calculated per gram of catalyst. At higher reaction temperature (350 °C), the catalyst CZA3 is the most active followed by catalysts B and A. At low reaction temperature (300 °C), the catalyst B provided the best results, closely followed by catalyst CZA3. It can be stated that catalyst B preserves its high activity even at low reaction temperatures, not differing too much from the activity observed at high reaction temperature.

The reason for the high activity of the catalyst B seems to be a higher number of active sites reducible in a lower temperature region (400–480 °C) than in other catalysts (see Table III).

On the other hand, results of the catalytic tests obtained under higher pressure with 1-benzothiophene as a model compound showed that activity of the CZA3 catalyst is higher than that of catalyst B and lower than the activity of the A catalyst. Catalytic tests using light gas oil performed under higher pressure gave quite a similar order of catalyst activities like 1-benzothiophene. The difference was observed with catalyst A, which showed a slightly lower activity than in the test with 1-bentzothiophene.

A comparison of the results from 1-benzothiophene and light gas oil HDS performed under higher pressures exhibited a similar tendency in the catalyst activities. The catalyst activities obtained in thiophene HDS under atmospheric pressure demonstrated a substantially higher catalytic activity of CZA3 than those observed for the industrial A and B catalysts. Similarly, Reinhoudt et al.[25] have observed differences in the activities of various hydrotreatment catalysts tested under atmospheric and higher pressures, using thiophene and dibenzothiophene. The differences should not be ascribed to the found differences to the nature of the sulfur compound but to the surface morphology of the catalysts. On the contrary, Ledoux et al.[26] reported a satisfactory correlation between the activity in thiophene conversion and dibenzothiophene HDS within the same family of catalysts (CoMo or NiMo). Qusro and Massoth[27] found out a similar correlation for a series of $Mo/Al_2O_3$ catalysts.

Examination of the CZA3 porous structure after testing in the pilot-plant unit documented an increase in BET surface area (see Table II) caused, very likely, by a partial coke deposition in the catalyst pores. Diminishing the pore radius was reflected in an increase in micropore volume. It should be mentioned that not only the pore size characteristics of the catalyst slightly changed after testing in the pilot-plant unit, but also the IR spectrum revealed significant transformations (see Fig. 2). Considerable broadening of all bands is observed which indicates stronger interaction of both Mo and Co species with the support surface and/or formation of a mixed CoMo phase. The absorption bands of different compounds very likely overlap in the spectrum. The phases observed in the catalysts seem to be similar, only their concentration in catalyst CZA3 is lower. That is why the spectrum is enlarged and the bands are not fully separated. The TPR data confirm similarity of the reducible phases observed in the catalysts but difference is in their concentration and dispersion.

The shoulders at ca 500, 900 and 1200 $cm^{-1}$ in the spectrum of the CZA3 catalyst appearing after catalyst testing in the pilot-plant unit, not found in the spectrum of the fresh catalyst confirm the formation of molybdates and sulfates in the catalyst[28].

## CONCLUSION

Cobalt–molybdenum catalysts on alumina synthesized using Co heteropolyoxomolybdate and additional Co show a high and sufficiently stable activity in HDS of different materials. The order of activities of the synthesized and industrial catalysts in conversion of 1-benzothiophene and light gas oil, as determined in a laboratory reactor at 1 MPa and in a pilot-plant unit at 3 MPa, respectively, are approximately the same if the activities are calculated relative to 1 mmol of catalytic active components. The order of catalyst activity obtained from thiophene conversion somewhat differed from those obtained under higher pressure. Differences among the catalysts were, however, higher than those observed under higher pressures and, therefore, the low-pressure tests with thiophene seem to be more sensitive. Nevertheless, this cannot give the exact answer how a new catalyst will behave under industrial conditions. The test is useful and satisfactory for relative comparison of catalyst activities.

The temperature-programmed reduction data obtained with all catalysts confirm the importance of the presence of easily reducible phase in the catalyst for a high catalyst performance. Catalyst B containing the highest amount of the phase reducible in the low-temperature range (20–600 °C) is the most active at the lowest reaction temperature. The TPR results obtained confirm that not only the number of active sites, but also facile reducibility of the $Mo^{6+}$ active sites is important for achievement of high HDS catalytic activity.

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