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# CoMo/$ZrO_2$ Hydrodesulfurization Catalysts Prepared by Chelating Agent Assisted Spreading

**Luděk Kaluža · Daniela Gulková · Zdeněk Vít · Miroslav Zdražil**

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**Abstract** The novel Mo/$ZrO_2$ and CoMo/$ZrO_2$ catalysts were prepared by impregnation of the monoclinic $ZrO_2$ by the chelating agent nitrilotriacetic acid (NTA) assisted spreading of $MoO_3$ with $CoCO_3 \cdot xH_2O$ and compared with samples prepared conventionally. The catalysts were characterized by X-ray diffraction, $N_2$ physisorption, $O_2$ chemisorption and activity in 1-benzothiophene hydrodesulfurization (HDS). The application of NTA during the catalysts preparation systematically increased the HDS activity by the factor 1.2–1.7.

**Keywords** CoMo/$ZrO_2$ · Monoclinic $ZrO_2$ · Benzothiophene hydrodesulfurization · Chelating agent assisted spreading

## 1 Introduction

Increasingly stringent regulations on sulfur level in liquid fuels have been recently driving the research on highly active hydrodesulfurization (HDS) catalysts. The conventional CoMo catalysts are supported onto $\gamma$-$Al_2O_3$ and they are prepared by the consecutive or simultaneous impregnation of the support with aqueous solutions of ammonium heptamolybdate (AHM) and cobalt nitrate followed by calcination and sulfidation. The addition of chelating agents [1–17] such as of nitrilotriacetic acid (NTA) or ethylenediaminetetraacetic acid (EDTA) into the impregnating solution often resulted in increased HDS activity.

One explanation in the literature is the following. Complex of chelating agent with Co or Ni is formed. This stabilizes Co or Ni against sulfidation so that they are sulfided after Mo. The result is larger number of Co and Ni atoms decorating $MoS_2$ crystals, which is important for activity promotion. In the absence of chelating agent, Co and Ni are sulfided before Mo and this leads to formation of inactive bulk Co and Ni sulfides [1–5]. However, the phenomenon was observed also for silica supported Co catalyst for Fischer–Tropsch synthesis, where sulfidation is not involved. So, alternative explanation comes into account. Complex formation influences the interaction of metal species with the support and results in increased dispersion of metal compound after calcination [6, 7]. The phenomenon has already been described for CoMo and NiMo supported on pure active carbon [8, 9], alumina [8, 10–15], silica [1, 16, 17], modified $\gamma$-$Al_2O_3$ [18], and wide-pore mixed $ZrO_2$–$TiO_2$ [19].

Nevertheless, the original method of the preparation of the impregnating solution containing chelating agent is rather complicated. Chelating agent is usually dissolved in $NH_4OH$, the solid $MoO_3$ is added and the mixture is heated until all $MoO_3$ dissolves. In the end, Co(Ni) nitrate is added and dissolved [17]. Alternatively, the impregnation solution is made from AHM, cobalt nitrate and NTA [13, 20, 21].

In contrast, we have previously found an unconventional method of CoMo deposition using water slurries of low solubility precursors such as $MoO_3$ and cobalt carbonate hydrate. We applied the water-assisted spreading method (WAS) also on an alternative support $ZrO_2$. For example, $MoO_3$ was spread onto $ZrO_2$ in water to form the saturated adsorption monolayer with density of 3.4 Mo atoms per

L. Kaluža (✉) · D. Gulková · Z. Vít · M. Zdražil
Institute of Chemical Process Fundamentals of the Academy of Sciences of the Czech Republic, v.v.i., Rozvojová 135, Suchdol, 16502 Prague 6, Czech Republic
e-mail: kaluza@icpf.cas.cz

$nm^2$ [22]. After deposition of Mo, the point of zero charge decreased from about 7.3 for $ZrO_2$ to about 2.4 for a $MoO_3/ZrO_2$ catalyst, which was close to the point of zero charge of $MoO_3$ (2.1) [23]. This decrease allowed the subsequent deposition of low solubility cobalt carbonate for promotion of HDS activity (pH of the slurry $CoCO_3/H_2O$ was about 8.6 and dissolved Co cations well adsorbed onto the negatively charged surface of $MoO_3/ZrO_2$) [19]. It was found that only the monoclinic form of $ZrO_2$ (108 $m^2/g$, baddeleyite) led to highly active catalysts while the use of amorphous or the mixture of tetragonal and monoclinic $ZrO_2$ led to catalysts with low HDS activity [22].

The aim of the present work was to study the deposition of Co and Mo with the use of the chelating agent NTA onto the monoclinic form of $ZrO_2$. Firstly, the addition of NTA to form aqueous impregnation solutions from AHM and cobalt nitrate was investigated and this new method was compared with Co and Mo deposition by conventional subsequent aqueous impregnation. Secondly, the possibility of employing the chelating properties of NTA to form impregnation solution from $MoO_3$ and cobalt carbonate hydrate was studied and the approach was compared with the WAS method. These two new preparation procedures of $CoMo/ZrO_2$ catalysts have not been reported in the scientific and patent literature up to now and they are thus of high research interest. The prepared catalysts were characterized by powder X-ray diffraction, nitrogen physisorption and oxygen chemisorption. Their activities were determined in HDS reaction of 1-benzothiophene (BT) and they are compared with that of industrial reference catalysts supported on $Al_2O_3$.

## 2 Experimental

The $ZrO_2$ extrudates (Alfa Aesar, product no. 043815, Germany, S(BET) = 108 $m^2/g$, V(p) = 0.26 $cm^3/g$) were crushed and sieved to particle size fraction 0.16–0.32 mm. Co and Mo were deposited onto the support to achieve the Mo content corresponding to 3.5 at.Mo/$nm^2$, and the Co content corresponding to Co/(Co+Mo) molar ratio of 0.3. Four methods were used: (1) conventional impregnation from solution of well soluble Co and Mo salts (CIM), (2) WAS of poorly soluble precursors, (3) impregnation from solution of NTA and the well soluble salts (CIM–NTA), and (4) water-assisted spreading of poorly soluble precursors with the assistance of NTA (WAS–NTA).

1. The support (5 g) was mixed with aqueous solution of AHM (20 ml) and it was shaken for 1 h. It was dried in rotary vacuum evaporator at 95 °C for 1 h and calcined in air flow at 400 °C for 1 h with a temperature ramp of 6 °C/min. The sample was labelled Mo(CIM). Part of it (2.5 g) was then impregnated with the solution of $Co(NO_3)_2$ (10 ml), and it was dried and calcined in the same way. The catalyst was labelled CoMo(CIM)
2. The support (5 g) was allowed to react with $MoO_3$ (Aldrich, product no. 69850, Czech Republic, ground in planetary mill for 24 h) in 20 ml of the aqueous slurry under reflux at 95 °C. After 1.5 h, solid $MoO_3$ disappeared from the slurry, the sample was dried in vacuum evaporator at 95 °C for 1 h and labelled as Mo(WAS). Part of it (2.5 g) was then allowed to react with 10 ml of the aqueous slurry containing $CoCO_3$ (cobalt carbonate hydrate, Aldrich, product no. 202193, 46.2 wt% Co, ground in planetary mill for 24 h) under the same conditions and it was labelled as CoMo(WAS)
3. The support (5 g) was immersed into 20 ml of the aqueous solution containing the AHM, cobalt nitrate and NTA for 1 h. The sample was dried in vacuum evaporator at 95 °C for 1 h but it was not calcined. The samples CoMo(CIM–NTA$^a$) with NTA/Co = 1 and CoMo(CIM–NTA) with NTA/(Co+Mo) = 1 were prepared
4. The mixture of the $MoO_3$, $CoCO_3$, and NTA with molar ratio NTA/(Co+Mo) = 1 was gradually dissolved in 20 ml of water at 60 °C in about 0.5 h. Of the support (5 g) was then immersed into this solution and the slurry was mixed for 1 h. The sample was dried in vacuum evaporator at 95 °C for 1 h and labelled as CoMo(WAS–NTA)

The following industrial $\gamma$-$Al_2O_3$ supported catalysts were used for comparison: Mo(BASF) containing 15.0 wt% $MoO_3$ ($Mo/Al_2O_3$, M8-30, BASF, Germany) and CoMo(KF756) containing 3.2 wt% CoO and 15.5 wt% $MoO_3$ ($CoMo/Al_2O_3$, KF 756, Albemarle, the Netherlands).

The X-ray diffraction data were measured using a Philips X'Pert MPD system in Bragg–Brentano reflecting geometry using Co K$\alpha$ radiation (40 kV, 30 mA) with wavelength 0.178897 nm and a secondary graphite monochromator. The data were collected in the range of 10–80° 2 $\theta$, at the rate of measurement of 0.02° per 1.6 s.

$N_2$ adsorption isotherms were measured over the support and reference catalysts using an ASAP 2010M instrument (Micromeritics, USA). Before the measurement, the samples were evacuated at 110 °C for 12 h. Specific surface area, S(BET), was determined by the Brunauer–Emmett–Teller (BET) procedure. The total pore volume, V(p), of the support was calculated from the amount of $N_2$ adsorbed at $p/p_0 = 0.98$. The specific surface area of the prepared catalysts (dried in a rotary vacuum evaporator at 95 °C) and these catalysts after sulfidation (details of the sulfidation procedure are given below) was determined by the method of Nelsen and Eggersten [24] in $N_2$/He mixture (20/80) in a FlowSorp III instrument (Micromeritics, USA) using the $ZrO_2$ support and its S(BET) as a reference. Before the measurement, all samples were dried in the gaseous $N_2$/He mixture (Linde Gas a.s., Czech Republic) at 110 °C for 1 h.

Oxygen chemisorption [25] was performed over the sulfided catalysts (details on the sulfidation procedure are provided below) flushed by helium (Linde AG, 6.0, Germany) at 400 °C for 1 h and cooled in a mixture of dry ice and ethanol. The amount of chemisorbed $O_2$ was determined from pulses of $O_2$ (Linde Gas a.s., Czech Republic) added to the flow of He, which was monitored with a thermal conductivity detector VICI (Valco Instrument Inc., USA) and an HP 3394A integrator (Hewlett Packard, USA).

HDS of 1-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. Before the measurements, the catalysts were sulfided in a $H_2S/H_2$ flow (1/10) at 400 °C and atmospheric pressure with a temperature ramp of 6 °C/min and a dwell time of 1 h. The composition of the feed was kept constant at 16, 200 and 1,384 kPa of BT, decane and hydrogen, respectively. The catalyst weight, $W$, was varied 0.02–0.2 g depending on the catalyst activity and it was diluted with an inert corundum to form a bed length of 30 mm. The reaction was run at three feed rates, $F$, of BT including 7.7, 10.3 and 15.5 mmol/h. Steady state was reached in 30 min after each change in the feed rate. The reaction mixture was analyzed on a gas chromatograph (Hewlett Packard, 6890 series, Germany) equipped with a capillary column (HP-5, 30 m, 0.53 mm, 1.5 μm). 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 $a(\mathrm{BT}) = 1-x(\mathrm{BT}) = n(\mathrm{BT})/n_0(\mathrm{BT})$, $a(\mathrm{EB}) = x(\mathrm{EB}) = n(\mathrm{EB})/n_0\ (\mathrm{BT})$, $a(\mathrm{DH}) = x(\mathrm{DH}) = n(\mathrm{DH})/n_0(\mathrm{BT})$, where $n_0$(BT), $n$(BT), $n$(EB), and $n$(DH) are the initial number of moles of BT and final number of moles of BT, EB, and DH, respectively. The empirical pseudo-first-order rate constants of ethylbenzene formation $k$(EB) were calculated from the dependence of the relative composition $a$(EB) within the range 0.05–0.95 on space time $W/F$ and it was normalized per mol of Mo or Co + Mo in Mo or CoMo catalysts, respectively.

## 3 Results and Discussion

### 3.1 Concept of Co and Mo Deposition

The Co and Mo are usually deposited onto $ZrO_2$ supports by subsequent impregnation (Mo first, Co second) because AHM and cobalt nitrate normally precipitate in aqueous solutions to form cobalt molybdates. Furthermore, calcination at temperature above 350 °C [26] is needed after Mo deposition to decompose the Mo salt prior to Co deposition. It was found that the presence of NTA in both studied concentrations in the impregnation solutions prevents the precipitation reaction. The impregnation method with the use of NTA is thus convenient to deposit the metals onto $ZrO_2$ in one impregnation step. Furthermore, the chelating properties of NTA were so strong that they allowed the dissolution of $MoO_3$ (solubility in water is only 1.2 g per 100 ml at 60 °C [27]) and, surprisingly, also the dissolution of the mixture of $MoO_3$ and $CoCO_3$. It was thus possible to deposit the precursors onto the $ZrO_2$ in one impregnation step. Another advantage of this method was that addition of $NH_4OH$ was not needed. Ammonia forms ammonium sulfide during in situ sulfidation, which leads to plugging of the reaction apparatus if the reactor exit is not sufficiently heated.

The textural and structural parameters of the samples after the Mo and CoMo depositions were studied by $N_2$ physisorption and X-ray diffraction. The surface area of the support, prepared and reference catalysts is summarized in Table 1 and the selected X-ray diffraction patterns in Fig. 1.

It was found that subsequent deposition of Mo and Co by conventional impregnation from solution of AHM and cobalt nitrate (the samples Mo(CIM), CoMo(CIM)) or by WAS of $MoO_3$ and $CoCO_3$ (the samples Mo(WAS), CoMo(WAS)) onto the $ZrO_2$ as well as drying or sulfidation of the samples did not significantly influenced the specific surface area. In contrast, the presence of NTA decreased the surface areas in dried samples (Mo(WAS–NTA), CoMo(CIM–NTA[a]), CoMo(CIM–NTA),

**Table 1** Specific surface areas of the support, prepared and reference catalysts

| Sample | Specific surface area ($m^2$/g) | |
|---|---|---|
| | Dried (95 °C) | Sulfided (400 °C) |
| $ZrO_2$ | 108[i] | 108 |
| Mo(CIM) | 112 | 108 |
| Mo(WAS) | 118 | 106 |
| Mo(WAS–NTA) | 79 | 119 |
| CoMo(CIM) | 106 | 94 |
| CoMo(WAS) | 115 | 116 |
| CoMo(CIM–NTA[a]) | 78 | 100 |
| CoMo(CIM–NTA) | 43 | 114 |
| CoMo(WAS–NTA) | 55 | 108 |
| Mo(BASF) | 198[i] | 121 |
| CoMo(KF756) | 264[i] | – |

[i] By BET method

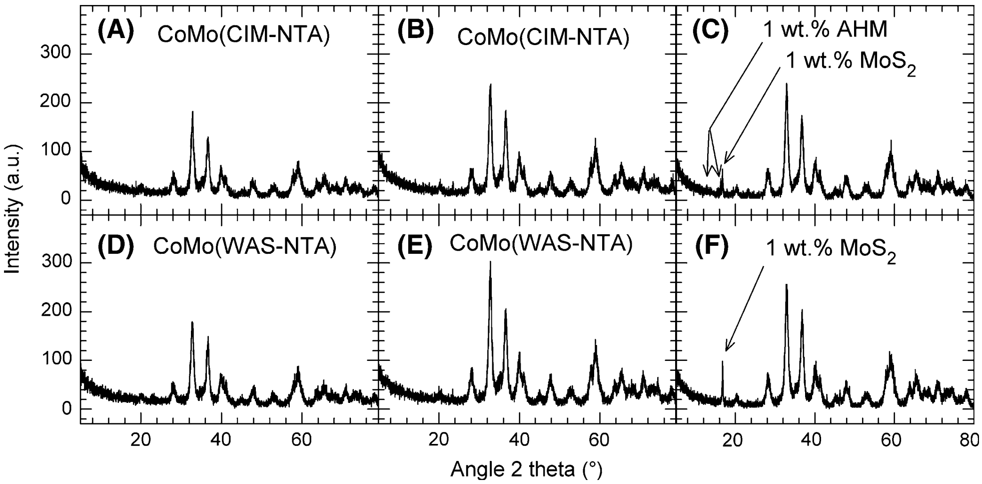

**Fig. 1** X-ray diffraction patterns. **a, d** catalysts dried in a rotary vacuum evaporator at 95 °C. **b, e** Catalysts sulfided in $H_2S/H_2$ at 400 °C. **c** Mechanical mixture (1 wt% AHM, 1 wt% $MoS_2$ and 98 wt% $ZrO_2$). **f** Mechanical mixture (1 wt% $MoS_2$ and 99 wt% $ZrO_2$)

CoMo(WAS–NTA)). After sulfidation, however, the high surface areas (99–119 $m^2/g$) were recovered. X-ray diffraction did not detect presence of crystalline phase of NTA, Mo or Co species in the catalysts after drying or sulfidation. Only the monoclinic phase of $ZrO_2$ (baddeleyite) was found.

To elucidate on the amount of active sites of the prepared sulfide phase, which is generally believed to be associated with degree of coordinative unsaturation and the amount of chemisorbed oxygen, the oxygen chemisorbed is given in Table 2. It was ascertained that the $ZrO_2$ support increased the amount of chemisorbed $O_2$ over the deposited metal sulfides more than two times in comparison to $\gamma$-$Al_2O_3$ support in industrial reference catalysts. Over the $ZrO_2$ supported catalysts, the lowest amount of chemisorbed $O_2$ was achieved for CoMo(CIM), which is probably connected with the loss of the metals from the surface to subsurface during calcinations. The Mo sample prepared with the assistance of NTA exhibited also only about 60 % of the chemisorbed $O_2$ of other two Mo catalysts. All CoMo catalysts prepared with the assistance of NTA exhibited by about 11–24 % lower amount of chemisorbed $O_2$ than CoMo catalyst prepared by water-assisted spreading CoMo(WAS).

**Table 2** Activity in HDS of BT at 360 °C and chemisorbed $O_2$ over the prepared and reference catalysts

| Sample | Adsorbed $O_2$ (mmol($O_2$)/mol(Me))$^i$ | $k$(EB) (mol(EB)/mol(Me)h)$^i$ |
|---|---|---|
| Mo(CIM) | 65 | 51 |
| Mo(WAS) | 75 | 58 |
| Mo(WAS–NTA) | 41 | 54 |
| CoMo(CIM) | 31 | 107 |
| CoMo(WAS) | 72 | 182 |
| CoMo(CIM–NTA$^a$) | 64 | 144 |
| CoMo(CIM–NTA) | 55 | 181 |
| CoMo(WAS–NTA) | 60 | 222 |
| Mo(BASF) | 16 | 27 |
| CoMo(KF756) | 22 | 282 |

$^i$ Me represents Mo or Co + Mo in the Mo or CoMo catalysts respectively

## 3.2 HDS Activity

The activities of the prepared and reference catalysts were determined in HDS of 1-BT. During 1-BT HDS, DH is formed by C=C bond hydrogenation (HYD) of BT. Ethylbenzene (EB) and $H_2S$ is formed by hydrogenolysis (HYG) of C–S bond of DH and BT. The HDS activities of the catalysts were therefore expressed as pseudo-first order rate constants of ethylbenzene formation $k$(EB) in Table 2 and selectivities to DH (HYD/HYG selectivities) were shown as a dependence of DH conversions $x$(DH) on BT conversions $x$(BT) in Fig. 2. A comparison of the HDS activities and the amount of chemisorbed $O_2$ is displayed in Fig. 3.

It was found that Mo catalysts supported on the $ZrO_2$ exhibited about 2 times higher HDS activity than the Mo

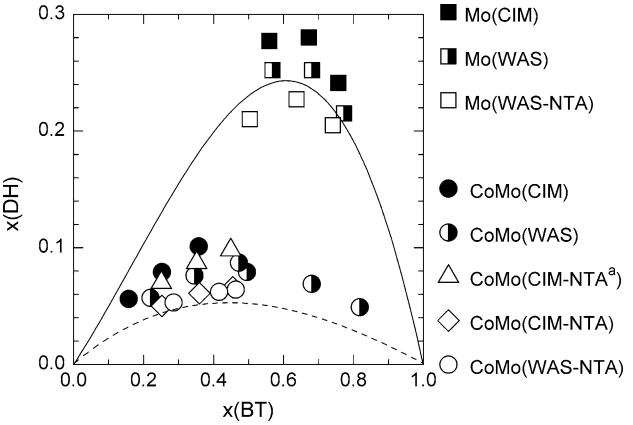

**Fig. 2** Selectivity to DH during 1-BT HDS. *Solid line* Mo(BASF); *dash line* CoMo(KF756)

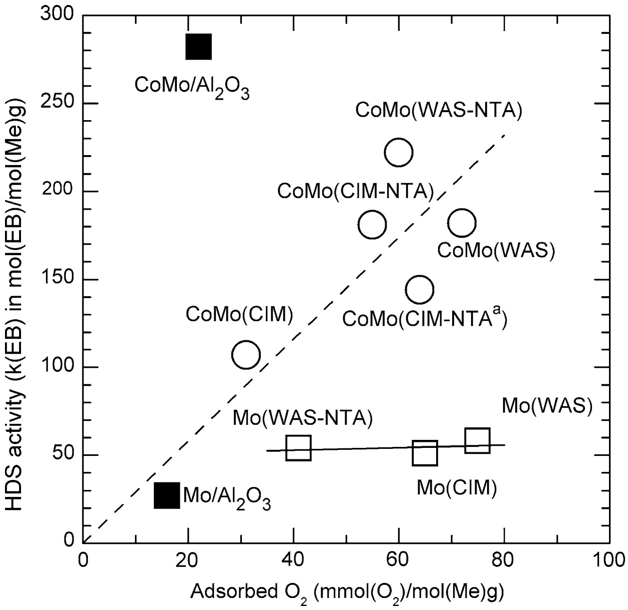

**Fig. 3** A comparison of HDS activity and amount of adsorbed O$_2$. *Filled squares* reference industrial Al$_2$O$_3$ supported catalysts; *open squares* and *solid line* ZrO$_2$ supported Mo catalysts; *open circles* and *dash line* ZrO$_2$ supported CoMo catalysts

catalyst supported on $\gamma$-Al$_2$O$_3$ (M8-30, BASF, Germany), which corresponded well to about two times higher dispersion (amount of adsorbed O$_2$). The use of NTA, however, decreased the MoS$_2$ dispersion (evaluated by the amount of adsorbed O$_2$) in Mo/ZrO$_2$ catalyst about 1.6 times despite keeping the twofold activity (Table 2; Fig. 3). It was concluded, that the method of Mo deposition did not significantly influence the resultant activity. The activity of Mo(WAS) was only slightly higher than that of Mo(WAS–NTA) and Mo(CIM). All prepared Mo catalysts exhibited high selectivity to DH, which was practically the same as that achieved over the reference Mo/Al$_2$O$_3$ catalyst. The activity data of Mo in BT HDS corroborated the previous studies of the HDS of thiophene [28–31] and dibenzothiophene [32], wherein Mo species supported on zirconia were at least twice as active as those supported on alumina.

In bimetallic CoMo catalysts supported on ZrO$_2$, the concentration of NTA and nature of the starting compounds influenced the resultant HDS activity. The catalysts exhibited more than twofold higher HDS activity and more than twofold lower selectivity to DH than the Mo counterparts. The promotion effect of Co on activity of the prepared catalyst was expressed as a ratio of $k$(EB) of CoMo catalyst and the $k$(EB) of Mo catalyst.

The promotional effect was the lowest for the catalyst prepared by consecutive impregnation deposition of AHM and cobalt nitrate, CoMo(CIM), possessing the value about 2.1. Applying the consecutive deposition by water-assisted spreading, CoMo(WAS), from the aqueous slurries of MoO$_3$ and cobalt carbonate hydrate, the promotional effect significantly increased to 3.1. The selectivity HYD/HYG qualitatively followed that trend. The higher promotional effect and HDS activity was accompanied with the decreased selectivity to DH.

After employing the NTA, the promotional effects varied within 2.8–4.1. The promotional effect was 2.8 and 3.6 when the concentration of NTA increased from NTA/Co = 1 to NTA/(Co+Mo) = 1, respectively. Again, the selectivity to DH was slightly lower over the catalyst with high HDS activity CoMo(CIM–NTA) than over CoMo (CIM–NTA$^a$) accompanied with low HDS activity. The highest HDS activity and promotional effect 4.1, however, was achieved over the catalyst prepared by NTA assisted spreading of MoO$_3$ and CoCO$_3$, CoMo(WAS–NTA). The selectivity to DH was the lowest and about the same as for the sample CoMo(CIM–NTA).

The approximate linear correlation between HDS activity and amount of chemisorbed O$_2$ was observed for all CoMo/ZrO$_2$ catalysts in Fig. 3. However, the point for CoMo/Al$_2$O$_3$ catalyst strongly deviates from this correlation. This corresponds to experience reported in the previous literature. The reasonable correlation HDS activity-adsorbed amount of O$_2$ was generally observed only for a family of closely related Co(Ni) Mo catalysts [33]. An example of the unsuccessful attempt to correlate HDS activity – O$_2$ chemisorption data in a set of seven industrial NiMo/Al$_2$O$_3$ catalysts could be found elsewhere [34].

It was ascertained that the use of NTA in impregnation solution systematically increased the HDS activities of CoMo/ZrO$_2$ catalysts by the factor 1.2–1.7. The preferred amount of NTA for high HDS activity promotion was NTA/(Co+Mo) = 1. The NTA increased the HDS activity 2.1 and 1.6-fold for the catalysts catalyst prepared from MoO$_3$ and CoCO$_3$ by WAS and from AHM and cobalt nitrate by CIM, respectively, in comparison to the catalyst prepared by conventional subsequent deposition of AHM and cobalt nitrate without the use of NTA. This increase newly obtained for the monoclinic ZrO$_2$ support is quite similar as those obtained previously for Al$_2$O$_3$ or SiO$_2$. For example, the catalyst prepared from NTA, AHM, and Al$_2$O$_3$ supports led to about 1.6 [8] and 1.2 [14] fold higher activity in HDS of thiophene and BT, respectively, than the catalyst prepared for comparison without the use of NTA. The catalyst supported on SiO$_2$ prepared form NTA, NH$_4$OH, MoO$_3$ and nickel nitrate resulted in about 1.5-fold higher activity in HDS of thiophene than that prepared without NTA [1].

Among ZrO$_2$ supported catalysts, the highest HDS activities of CoMo(WAS–NTA) and CoMo(CIM–NTA) were accompanied with the lowest selectivities to DH. (The differences between CoMo/ZrO$_2$ in Fig. 2 were not large but distinctly higher than the experimental error.) The amounts of chemisorbed $O_2$ over these catalysts were systematically lower than those achieved over the catalysts prepared by WAS without the use of NTA. These data suggested that the use of NTA led to formation of high quality of CoMoS active sites but it did not positively influence the number of active sites.

Nevertheless, the highest HDS activity achieved over CoMo(WAS–NTA) prepared from $MoO_3$ and $CoCO_3$ represented only about 80 % activity of the commercial CoMo/$Al_2O_3$ catalyst KF 756 despite the fact that the commercial catalyst adsorbed quite low amount of $O_2$ (Fig. 3). Because the studied $ZrO_2$ exhibited only 108 $m^2$/g (i.e. only 41 % of the specific surface area of the industrial catalyst KF 756 with 264 $m^2$/g), it could be expected that further improvement of catalytic activity can be achieved by increasing the surface area of the monoclinic $ZrO_2$. Higher specific surface area should disperse more active phase and so the HDS activity of the alumina supported catalysts would be overhelmed. The recent progress in increasing surface area of unconventional supports of HDS catalysts was summarizes in the review [35]. The promising synthesis of the high surface area $ZrO_2$ was also reported elsewhere [36, 37]. Our previous results [23], suggest, that for application in Co(Ni) Mo/$ZrO_2$ HDS catalysts, not only the surface area and pore distribution, but also crystalline phase is important. The employing of chelating agent NTA represents a promising way of preparation of highly active CoMo phase onto the monoclinic $ZrO_2$ support.

## 4 Conclusion

It was found that the use of chelating agent NTA during preparation of CoMo catalysts supported on the monoclinic $ZrO_2$ increased the HDS activity within the range 22–69 %. The molar ratio NTA/(Co+Mo) to achieve high HDS activities was 1/1. The most active CoMo/$ZrO_2$ catalyst was prepared by the impregnation of the support from the solution made by dissolution of $MoO_3$, $CoCO_3$ and NTA in water followed by sulfidation without previous calcination.

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