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Deposition of Co onto Supported MoS_2 by Water-Assisted Spreading: Increased Activity Promotion in Hydrodesulphurization of 1-Benzothiophene

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Abstract: Hydrodesulphurization (HDS) catalysts were newly prepared by water-assisted spreading of $CoCO_3.Co(OH)_2$ of low solubility in water onto pre-sulphided Mo species supported on several Al_2O_3 of surface area S_{BET} 77-262 m^2g^{-1}, ZrO_2 of S_{BET} 108 m^2g^{-1}, and TiO_2 of S_{BET} 140 m^2g^{-1}. The spreading was followed by scanning electron microscopy (SEM-EDX). X-ray photoelectron spectroscopy (XPS) and temperature programmed reduction (H_2-TPR) characterized partial re-oxidation of sulphidic Mo catalysts before Co sorption. The prepared catalysts were characterized in sulphidic form by H_2-TPR. Activity of catalysts was determined in the HDS reaction of 1-benzothiophene. The spreading of Co onto sulphidic catalysts led to systematic increase of HDS activity by 16–86% in comparison to the spreading of Co onto oxide samples.

Keywords: HDS; CoMo catalyst; water-assisted spreading; promotion; sulphidic Mo

1. Introduction

Sulphidic $CoMo/Al_2O_3$ catalysts represent typical heterogeneous catalysts developed for industrial hydrodesulphurization (HDS) reactions over the past 70 years [1]. Due to their key role in sustainable crude-oil processing, their structure, function, or synthesis are thoroughly investigated. The important phenomenon in HDS reactions is the promotional effect of Co on the activity of supported Mo species. Novel preparation methods are thus introduced in the literature both to provide fundamental understanding of promotion and to gain pronounced activity in HDS. One direction of this endeavor represents the examination of chelating agents for deposition of the CoMo phase [2–4]. Another direction of advanced syntheses is represented by direct deposition of Co onto sulphide Mo surface instead of promoting oxidic Mo surface [5–12].

For example, Bezverzkyy et al. [5] prepared $MoS_2/\gamma\text{-}Al_2O_3$ from aqueous solution of $(NH_4)_2MoS_4$ by reduction with N_2H_4 and special treatment in acetone. Deposition of Co was done using aqueous solution of cobalt nitrate or methanol solution of Co-acetylacetonate. Acetonic solutions of cobalt nitrate were used for the promotion of sulphided Mo species supported on TiO_2 and ZrO_2 or co-precipitated mixed Ti–Zr oxides by Ji [6] or Afanasiev [7], respectively. Farag et al. [8] compared carbon-supported CoMo catalysts prepared from methanolic solutions of molybdenyl acetylacetonate, followed by sulphidation and deposition of cobalt acetylacetonate with those catalysts prepared by successive impregnation without a sulphidation step and by the equilibrium adsorption method. About 50% improvement of activity in HDS of dibenzothiophene was observed after promotion of pre-sulphided Mo catalysts. For a series of catalysts supported on TiO_2, the result

of promotion of pre-sulphided Mo was a 30–70% increase in the activity of thiophene HDS in comparison with the promotion of oxidic Mo [9]. Thirty percent improvement in benzothiophene hydrodesulphurization was achieved in our previous paper dealing with organized mesoporous Al_2O_3 [10] after deposition of Co-acetylacetonate from ethanolic solution onto a presulphided form of Mo rather than the oxide form.

Another method of efficient promotion of MoS_2 species supported on γ-Al_2O_3 employs a cobalt carbonyl as a precursor. Maugé et al. [11] introduced $Co(CO)_3NO$ to sulphided Mo/Al_2O_3 and thermally decomposed it prior to HDS reaction of thiophene at atmospheric pressure. They found that the ex-carbonyl catalysts are twice as active as a conventional $Co–Mo/Al_2O_3$ catalyst. Okamoto et al. [12] observed a similar effect. The promotion of sulphidic Mo using $Co(CO)_3NO$ resulted in about 2-fold higher activity in HDS of thiophene than the activity achieved after promotion of oxidic Mo counterparts.

The promotion of supported Mo sulphide is thus also investigated in the present work applying, for the first time, the principle of our original method called water-assisted spreading (WAS). The method is based on gradual spreading of precursors almost insoluble in water such as MoO_3 or $CoCO_3.Co(OH)_2$. The point of zero charge of Al_2O_3 (PZC) is about 7 and the pH of MoO_3/H_2O slurry is 2.5; the sorption of dissolved anionic Mo species onto positively charged support is strong. This sorption proceeds up to the complete saturation of a support surface. The saturated adsorption loading of 3.4 Mo per nm^2 was achieved in our previous paper for the Al_2O_3 supports with surface area (S_{BET}) ranging from to 11 to 279 m^2g^{-1} [13]. Once the saturated MoO_3/Al_2O_3 catalysts are achieved, this oxidic form of catalysts (PZC of 2.8) can react with $CoCO_3.Co(OH)_2/H_2O$ slurry of pH about 8.5. Dissolved cationic Co species are gradually adsorbed onto negatively charged supported MoO_3 surface, and efficient promotion of activity in HDS of thiophene is observed [14].

The water-assisted spreading (WAS) is a clean method because it avoids using cobalt nitrate or ammonium heptamolybdate. Dried catalysts can be sulphided without calcination. Avoiding a calcination step is the other advantage of WAS. Comparing WAS with a previously reported method of thermal-assisted spreading (solid-solid wetting) [15–17], the main advantage of WAS is that application of the temperatures higher than 400 °C is avoided. Furthermore, the thermal-assisted spreading method has not been applied to spread Co species.

The aim of the present work is to elucidate whether the $CoCO_3.Co(OH)_2/H_2O$ slurry can also be used for efficient promotion of MoS_2 species (WAS_{sulph}). The studied supports, i.e., Al_2O_3 with S_{BET} range from 77 to 262 m^2g^{-1}, TiO_2 (S_{BET} of 140 m^2g^{-1}), and ZrO_2 (S_{BET} of 108 m^2g^{-1}), were selected from our previous studies [13,18]. The promotion effect of Co was determined in an HDS reaction of 1-benzothiophene at 1.6 MPa. The character of sulphidic Mo eligible for promotion by $CoCO_3.Co(OH)_2/H_2O$ slurry was described by measurement of point of zero charge (PZC), temperature programmed reduction (H_2-TPR), and X-ray photoelectron spectroscopy (XPS). Sorption of Co species was followed by scanning electron probe microanalysis (SEM-EDX). Deposition of Co over oxidic form of supported Mo species using $CoCO_3.Co(OH)_2/H_2O$ slurry (WAS_{ox}) or conventional impregnation with $Co(NO_3)_2/H_2O$ solution (CIM_{ox}) was done for comparison.

2. Results and Discussion

2.1. Concept of Co Deposition onto Sulphidic Mo Catalysts

The novel approach in the deposition of $CoCO_3.Co(OH)_2$ onto pre-sulphided Mo catalysts is suggested and explored in this study. Point of zero charge (PZC) of pre-sulphided Mo catalysts is mutually interrelated with the phenomenon of partial re-oxidation of sulphidic surface, which appeared crucial to carry on water-assistant spreading (WAS_{sulph}). Therefore, PZC and re-oxidation are discussed below comprehensively.

The point of zero charge (PZC) of sulphides is often reported to be low of about 2–3 and to be similar to elemental sulphur. However, this PZC often depends on the degree of hydration of the

sulphides and on partial re-oxidation of the surface. Furthermore, if a sulphidic phase is immersed in a solution or slurry of high pH, the partial re-oxidation of superficial sulphidic species to form $S_xO_y^{n-}$ is increased. [19]

We have observed that all freshly sulphided Mo catalysts (the catalysts were immersed into distilled water immediately after sulphidation) exhibited PZC values of about 7. This value was stable for some days if the mixture was not heated, stirred, or if the mixture was bubbled with nitrogen. The spreading of $CoCO_3.Co(OH)_2$ did not proceed. This is documented in Figure 1, wherein the content of Co is determined by SEM-EDX after selected time of reaction. Co content inside the extrudate body was zero for 14 days.

However, if sulphided Mo catalysts can oxidize with air, the PZC of these samples decreases to 4. This is caused just by stirring of the impregnation slurry, bubbling the slurry with air or heating the slurry under reflux condenser.

In order to consider how deep this partial re-oxidation of sulphided Mo catalysts is, we have performed H_2-TPR and XPS (Figure 2). These techniques were done after controlled re-oxidation of dried and sulphided Mo catalysts by ambient atmosphere. Raman spectroscopy [20–25] and O_2 chemisorption provided only additional information, and they are discussed in Supplementary Materials (Figure S1).

The examples, how H_2-TPR patterns of the partially re-oxidized Mo sulphides differ from the sulphidic phase, are shown in Figure 2a. Figure 2b,c show XPS spectra of Mo and S, respectively. Chemical state of these elements is summarized in Table 1. It was observed that partial re-oxidation of Mo sulphides is recognized after about 2 h exposure of the samples on air (Figure 2 and Table 1). The content of Mo^{6+} and SO_4^{2-} increased. TPR patterns differ significantly from the previous one. Despite the fact that partial re-oxidation of molybdenum sulphides on air presumably differs from re-oxidation in $CoCO_3.Co(OH)_2/H_2O$ slurry, both these re-oxidations caused decrease of PZC to 4 and most probably created adsorption centres for Co species.

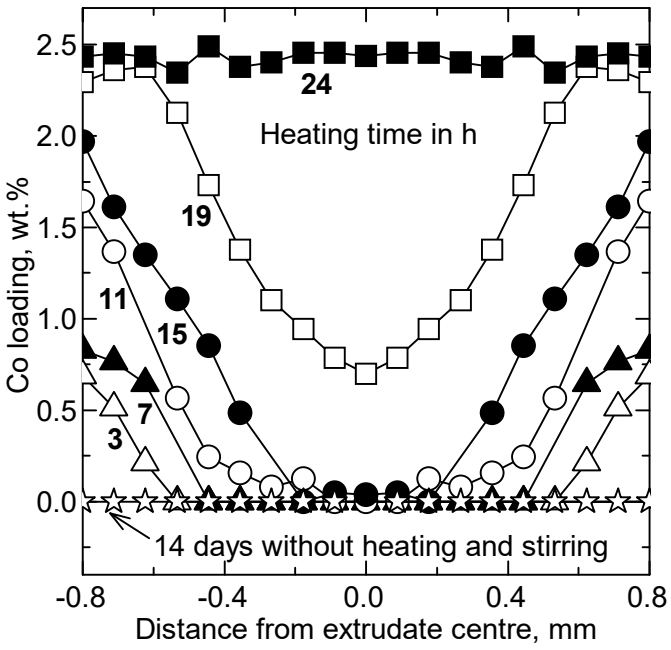

Figure 1. SEM-EDX analysis of Co content in bisected Mo/Al-262-e. Reaction of $CoCO_3.Co(OH)_2/H_2O$ slurry with sulphided Mo/Al-262-e at 95 °C.

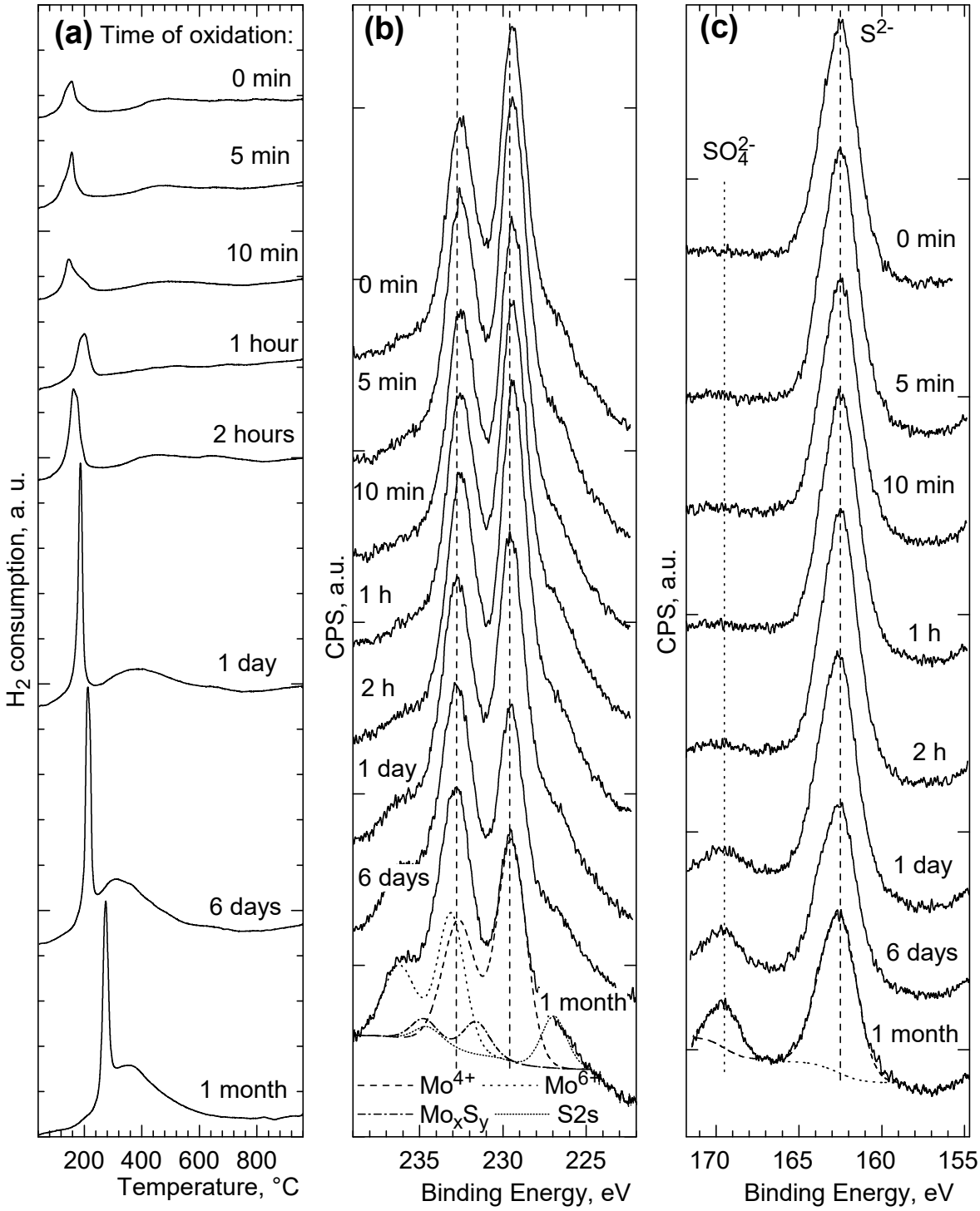

Figure 2. Re-oxidation of sulphided Mo/Al-262 on air followed by H_2-TPR (**a**) and XPS (**b**,**c**).

Table 1. XPS analysis of re-oxidation of sulphided Mo/Al-262 on air at laboratory temperature.

Oxidation	Atomic %						
Time	O 1s	Al 2p	Mo 3d			S 2p	
			Mo^{4+}	MoS_xO_y	Mo^{6+}	S^{2-}	S^{6+}
0 min	59.81	33.48	1.94	0.01	0.23	4.54	0
5 min	59.16	33.80	2.03	0.04	0.23	4.73	0
10 min	58.71	34.46	1.96	0.05	0.20	4.63	0
1 h	59.04	34.13	1.96	0.07	0.25	4.57	0
2 h	59.85	33.19	1.89	0.08	0.32	4.45	0.23

1 day	59.59	33.75	1.76	0.08	0.38	4.100.35
6 days	61.96	31.82	1.36	0.13	0.68	3.570.48
1 month	62.63	31.09	1.34	0.18	0.76	3.280.72

The continuation of our WAS_{sulph} experiment in Figure 1 shows how the sorption of Co from $CoCO_3.Co(OH)_2/H_2O$ slurry proceeded during heating and stirring of the mixture. The Co content inside the extrudates increased. Homogeneous and saturated concentration profile of Co was achieved after 24 h of spreading at 95 °C.

The saturation experiments over Mo/Al-262 and Mo/Al-262-e resulted in practically the same saturated adsorption loadings of Co with the value of about 2.5 wt.% (±0.1 wt%). The saturation of Mo/Zr-108-e and Mo/Ti-140-e with $CoCO_3.Co(OH)_2/H_2O$ slurry resulted in saturation adsorption loadings of Co 2.0 and 2.8 wt.% (±0.1 wt.%), respectively (Figure S3).

It was concluded that the PZC of 4 of sulphided and partially re-oxidized Mo catalysts is sufficiently low to allow the adsorption of Co^{2+} cations from $CoCO_3.Co(OH)_2/H_2O$ slurry of pH 8.5 onto negatively charged sulphidic surface. In principle, partial re-oxidation reaction is necessary and beneficial for the sorption of the Co^{2+} species because the negatively charged Mo sulphidic surface is needed. From a practical point of view, this re-oxidation does not need to be too deep. Heating on the water-bath together with $CoCO_3.Co(OH)_2/H_2O$ slurry and shaking of the mixture by bubbling air is sufficient to start this re-oxidation and successful performance of WAS_{sulph}.

The overview of actual loadings in all catalysts is presented in Table 2. The saturated adsorption loadings of Co by WAS_{sulph} were 15–50% higher than was achieved previously for promotion of supported MoO_3 monolayers [14]. Nevertheless, all loadings increased with increasing S_{BET}, and no crystalline phase of Co or Mo species in the catalysts was observed by XRD and Raman spectroscopy. The promotional effect of so deposited Co on HDS activity is discussed below.

Table 2. Survey of prepared catalysts: Saturated adsorption loadings of Mo and Co; Surface area S_{BET} of sulphided catalysts prepared by WAS_{sulph}; and Promotional effect of Co, PE, on activity of Mo catalyst in HDS of 1-benzothiophene.

Support	Loading, wt.% (±0.1)			S_{BET}, m^2g^{-1}	Promotional Effect PE (± 1.0)		
	Mo	Co	Co	(±5)	($PE = k_{EB}^{CoMo}/k_{EB}^{Mo}$)		
	WAS	[a]WAS_{ox}	[a]WAS_{sulph}	WAS_{sulph}	CIM_{ox} [b]	WAS_{ox}	WAS_{sulph}
Al-77	4.5	0.5	0.8	85	5.6	8.4	9.8
Al-78	4.1	0.4	0.8	81	4.5	5.7	7.8
Al-103	6.3	0.6	0.8	109	5.2	6.4	11.4
Al-127	7.4	1.0	1.2	131	5.4	7.6	13.7
Al-212	12.3	1.0	1.7	215	3.6	5.5	10.2
Al-262	14.3	2.0	2.4	244	3.4	6.3	11.8
Al-262-e	[c]14.3	-	2.4	249	-	-	11.1
Zr-108	6.0	1.3	2.0	101	3.2	4.1	8.0
Ti-140	7.9	2.0	2.8	130	4.0	4.1	6.3

[a] achieved in our previous studies [13,14]; [b] Co also deposited by CIM_{ox} with the same loading as it was achieved by WAS_{sulph}; [c] HDS activity measured after grinding and sieving to particle size 0.16–0.32 mm.

2.2. TPR and XPS of Sulphided Catalysts

All prepared catalysts were characterized in their sulphidic state by temperature programmed reduction (H_2-TPR) in Figure 3.

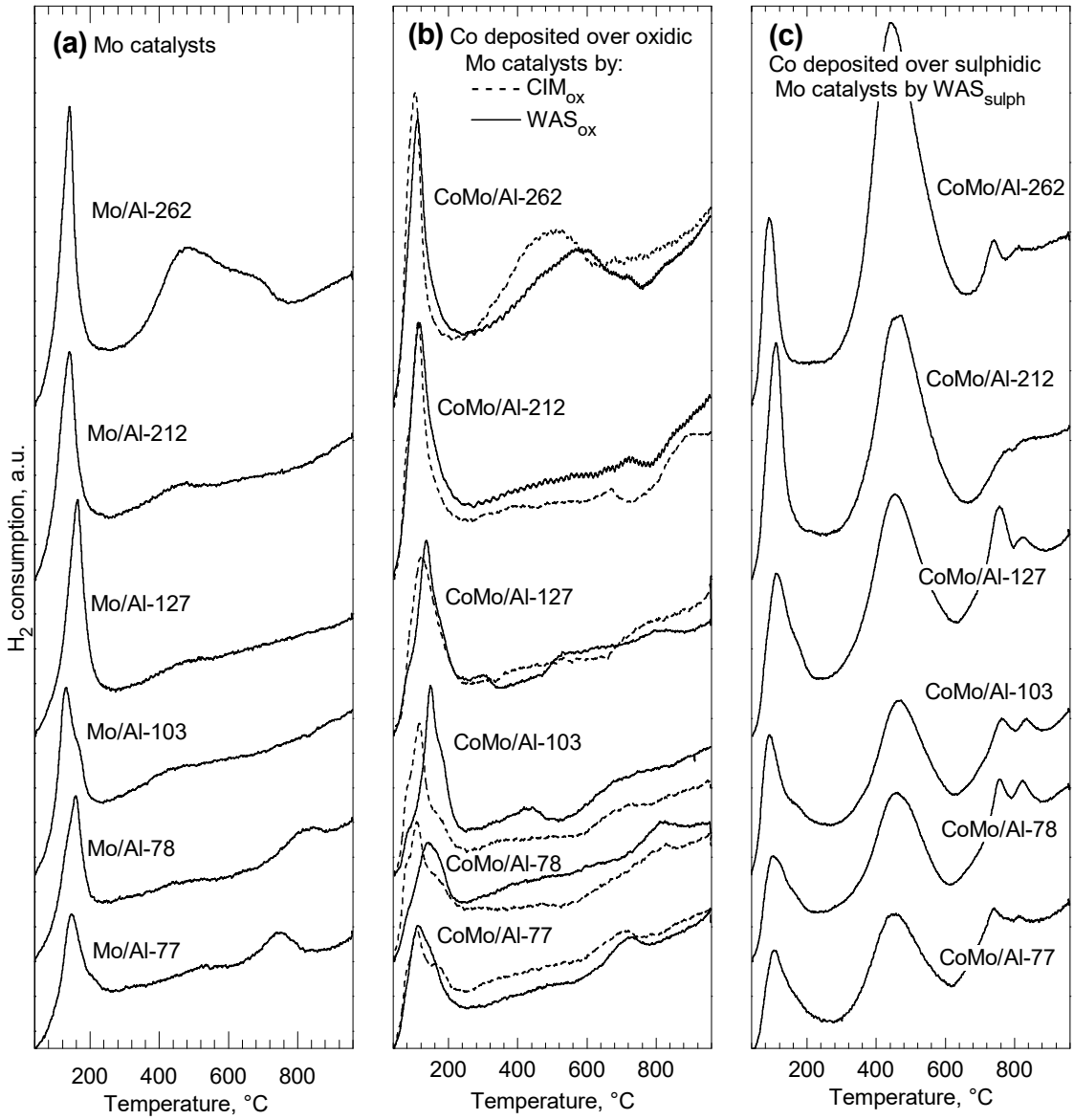

Figure 3. H_2-TPR patterns of sulphided (**a**) Mo, (**b**) CoMo (WAS_{ox}) and (CIM_{ox}), (**c**) and CoMo(WAS_{sulph}) catalysts.

The prepared Mo catalysts exhibited the first maxima at about 132–163 °C (Figure 3a). First low-temperature peaks typically appear between 179 and 185 °C [26] or 135–280 °C [27], and they are ascribed to the reduction of weakly bonded sulphur species such as S_2^{2-} edge moieties [28]. These species are believed to correspond with defects at MoS_2 edges. The quantity of these defects mostly depends on preparation procedure including support and activation conditions [27]. The second peak between 300 and 700 °C is typically less pronounced, and it belongs to elimination of less labile sulphur from the edges of the MoS_2 crystallites [29,30]. Because the method of preparation of our Mo catalysts was the same (WAS), the character of these defects was similar. We thus observed that the amount of these defects increased with increasing surface area of supports and therefore with saturated adsorption loadings of Mo (Table 2). The support only negligibly influenced the position of the first maxima. Nevertheless, the Mo/Al-262 with the highest surface area exhibited a pronounced second maximum (Figure 3a), which indicated the highest number of defected sites and/or the smallest MoS_2 crystallites (the highest MoS_2 dispersion) for the studied Mo catalysts. The direct link between the quantity of sulphur elimination during TPR and HDS activity has already

been reported, for example [1,31] We observed a relationship of a similar nature (HDS activity is discussed in Section 2.3.).

In the prepared CoMo catalysts, shifts of the first maxima to lower temperatures were caused by the promotion of Mo catalysts by Co (Figure 3b,c). These shifts are in agreement with previously reported results about TPR of CoMo catalysts [29,32]. DFT calculation explained this decrease by a weaker sulphur-metal bond energy in CoMoS than in MoS_2 [33]. We observed that the CoMo catalysts prepared by CIM_{ox} and WAS_{ox} exhibited the first maxima at 100–144 °C (Figure 3b). The CoMo catalysts prepared by WAS_{sulph} exhibited the first maxima at lower temperatures at 90–109 °C (Figure 3c). Moreover, the Co deposited by WAS_{sulph} caused a pronounced increase of the second reduction peak with maxima at about 450 °C. The WAS_{sulph} method thus distinctly increased the reducibility of the resulting catalysts. This could be caused by formation of specific CoMoS phase with a different character from CIM_{ox} or WAS_{ox} samples. WAS_{sulph} could promote the MoS_2 edges more efficiently than the other methods. The other explanation could be that the Co deposited by WAS_{sulph} could act differently during re-sulphidation, which could lead to smaller crystallites of CoMoS with lower slab length. Similar effects of Co were observed in TPR patterns of unsupported catalysts [34–36].

The three most active catalysts, i.e., CoMo(WAS_{sulph})/Al-262, CoMo(WAS_{sulph})/Al-212, and CoMo(WAS_{sulph})/Al-127, were evaluated in their sulphidic state by XPS. They were also compared with their counterparts prepared by the WAS_{ox} method. The comparison is shown in Table 3 and Supplementary Materials in Figure S5. It was found that the catalysts prepared by WAS_{sulph} had a higher Co/Mo ratio, a higher amount of Co in sulphidic state, and higher sulphur content on the surface than the other catalysts had. Superficial XPS analysis thus confirmed that Co loading achieved by WAS_{sulph} is higher than that achieved by WAS_{ox} (Table 2) and that Co deposited by WAS_{sulph} increases reducibility of the supported active species.

Table 3. XPS analysis of selected sulphided CoMo catalysts.

CoMo Catalysts	**Atomic %**								
	O 1s	**Al 2p**	**Co**		**Mo 3d**			**S 2p**	
			Co^{2+}_{ox}	Co^{2+}_{sulph}	Mo^{4+}	MoS_xO_y	Mo^{6+}	S^{2-}	S^{6+}
WAS_{sulph}/Al-262	59.84	30.89	0.56	1.32	1.69	0.52	0.24	5.99	0
WAS_{sulph}/Al-212	57.96	32.99	0.55	1.19	1.65	0.47	0.26	5.06	0
WAS_{sulph}/Al-127	57.24	33.05	0.37	0.95	0.82	0.33	0.16	4.02	0
WAS_{ox}/Al-262	57.72	32.96	0.74	0.33	1.60	0.56	0.37	5.70	0
WAS_{ox}/Al-212	58.02	34.13	0.50	0.23	1.56	0.50	0.27	4.80	0
WAS_{ox}/Al-127	58.73	35.50	0.47	0.33	0.75	0.38	0.17	3.27	0

2.3. HDS Activity

Figure 4 shows how the method of preparation and the surface area of original support influence the activity (k_{EB}) in 1-benzothiophene HDS.

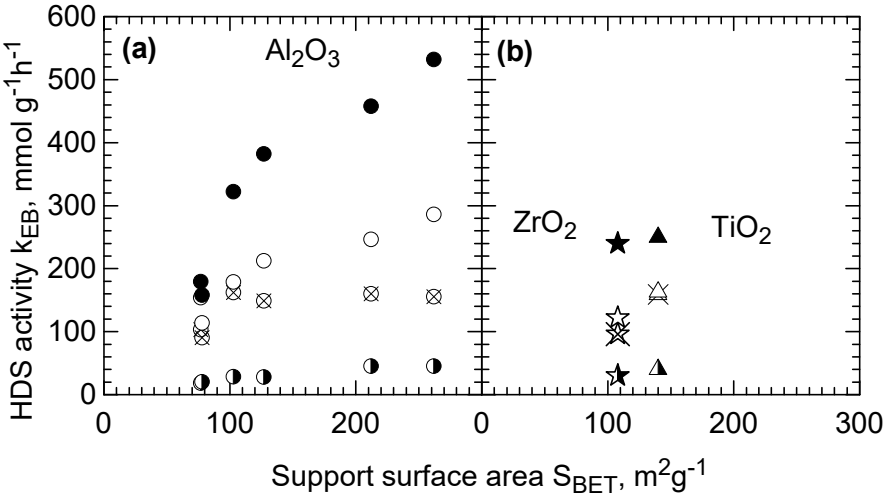

Figure 4. Activity of prepared catalysts k_{EB} in HDS of 1-benzothiophene at 360 °C and 1.6 MPa: (**a**) circles–Al_2O_3-supported catalysts; (**b**) asterisks–ZrO_2-supported catalysts, triangles–TiO_2-supported catalysts. Half-solid symbols–Mo catalysts, crossed symbols–CoMo(CIM_{ox}) catalysts, open symbols–CoMo(WAS_{ox}) catalysts, solid symbols–CoMo(WAS_{sulph}) catalysts. The k_{EB} of commercial CoMo catalyst was 421 mmol $g^{-1}h^{-1}$.

For each support, Co deposited over sulphidic Mo (WAS_{sulph} method) led to the catalyst with the highest HDS activity (Figure 4). The activity increase of 16–86% was systematic for all CoMo(WAS_{sulph}) catalysts. The most pronounced increase was observed for the catalysts supported on the aluminas with S_{BET} higher than 100 m^2g^{-1} or supported on the zirconia (more than about 80%). Co deposited over sulphidic Mo (WAS_{sulph} method) thus exhibited the highest promotional effect in Table 2. It was concluded that the method of preparation of CoMo catalysts increased the HDS activities in the order CIM_{ox} < WAS_{ox} < WAS_{sulph}.

The explanation could consist in the partial re-oxidation of MoS_2 catalysts during WAS_{sulph}. The partial re-oxidation of MoS_2 slabs creates sorption sites either at the edges of Mo slabs or at other defect sites of MoS_2 surface. Promotion of these sorption sites by Co was effective and essential for the HDS activity increase. These sorption sites are not presented on oxidic Mo monolayer. Therefore, the deposition of Co by conventional impregnation (CIM_{ox}) or water-assisted spreading (WAS_{ox}) leads to less active catalysts.

The effect of sulphidation and partial re-oxidation of sulphided Mo, CoMo and NiMo has also been studied in the previous literature [4,37,38]. The authors focused on resultant surface morphology and HDS activity. They concluded that partial re-oxidation and re-sulphidation slightly decreased the number of MoS_2 slabs with a length of 1–1.5 nm while the rest of the MoS_2 slabs (length of 1.5–7.0 nm) remained practically unaffected. At the same time, this treatment increased the activity of Mo catalyst in thiophene HDS by about 20%. For the CoMo catalyst, the same treatment increased the HDS activity more, by about 39%. We achieved similar increases in HDS activity, which can also be attributed to re-oxidation of the sulphide Mo phase.

Selectivity to dihydrobenzothiophene provides additional information on HDS of 1-benzothiophene to ethylbenzene (Figure 5). Yields of dihydrobenzothiophene over CoMo catalysts are compared in Supplementary Materials in Figure S6. It was found that the highest activity of CoMo(WAS_{sulph}) catalysts was also accompanied with the lowest selectivity to dihydrobenzothiophene. Co in CoMo(WAS_{sulph}) thus efficiently promoted the direct desulphurization (DDS) pathway (Figure 5).

It is also worth noting that the ZrO_2- and TiO_2-supported catalysts still did not reach activities of the alumina-supported counterparts. However, the increase of activity by the WAS_{sulph} method was significant (Figure 4, Table 2), but the selectivity to DDS was similar to other CoMo(WAS_{sulph}) catalysts (Supplementary Materials, Figure S6). It seems that this lack of promotion by Co is an intrinsic property of the ZrO_2– and TiO_2-supported CoMo catalysts [1,39].

It was concluded that water-assisted spreading of Co onto pre-sulphided Mo catalysts (WAS_{sulph}) represents a convenient way to utilize the surface area of supported Mo and enhance HDS activity. The most active catalyst 2.4Co14.3Mo(WAS_{sulph})/Al-262 was prepared over gamma-alumina Akzo (HDS-000-1.5, Akzo Chemicals, City, the Netherlands), and it was about 1.3-fold more active than the commercial CoMo catalyst.

3. Materials and Methods

3.1. Catalysts Preparation

3.1.1. Mo Deposition

Details about supports were described in our previous work [13,18], and the supports were named in the same way in the present paper. For example, the name Al-262 is used for Al_2O_3 with surface area S_{BET} of 262 m^2g^{-1}. All supports were crushed and sieved to particle size fraction 0.16–0.32 mm. Mo was deposited over support by WAS. MoO_3 (Fluka, product no. 69850, Buchs, Switzerland) was ground in stainless steel planetary mill (Fritsch, Pulverisette 6, Idar-Oberstein, Germany) for 24 h in order to increase its dissolution rate. MoO_3 was mixed with support (0.9 mg of MoO_3 per 1 m^2 of support) and distilled water. The mixture was heated under reflux condenser at 95 °C for 24 h. The unreacted slurry of MoO_3 was separated from catalyst particles by 5-time decantation with distilled water. Catalysts were dried in a rotary vacuum evaporator at 95 °C for 1 h and the Mo content was determined by atomic adsorption spectroscopy (AAS) in Table 2. Part of the sample was additionally sulphided in H_2S/H_2 mixture (molar ratio was 10:1) at 400 °C (ramp rate 6°C min^{-1} and dwell time 1 h). The sample was inserted into gas tight ampules under nitrogen.

3.1.2. Co Deposition

Co was deposited onto dried MoO_3 catalysts by conventional impregnation (CIM_{ox}) using aqueous solution of $Co(NO_3)_2$ or water-assisted spreading (WAS_{ox}) using aqueous slurry of $CoCO_3.Co(OH)_2$. $CoCO_3.Co(OH)_2$ was selected according to our previous research [14], where $CoCO_3.Co(OH)_2$ adsorbed onto supported MoO_3 catalysts the fastest from the studied compounds (Co_3O_4, $Co(OH)_2$, $CoCO_3$, $CoCO_3.Co(OH)_2$).

Aqueous solution of cobalt nitrate ($Co(NO_3)_2.6H_2O$, Lachema, purum, Brno, Czech Republic) was stirred with Mo catalyst for 1 h and then the mixture was dried in a rotary vacuum evaporator at 95 °C for 1 h. The obtained CoMo(CIM_{ox}) was calcined in air flow at 350 °C for 0.5 h and then sulphided (the sulphidation procedure was described above). The amount of Co was chosen to be equal to actual loading of Co achieved by the WAS_{sulph} method (Table 2).

Cobalt hydroxide carbonate ($CoCO_3.Co(OH)_2$, Merck, reinst, Buchs, Switzerland) was ground in the stainless steel planetary mill for 24 h. Aqueous slurry of the compound with MoO_3 catalyst was heated under reflux condenser at 95 °C for 24 h. The nominal amount of 0.1 g of $CoCO_3.Co(OH)_2$ was used to saturate 1 g of dried MoO_3 catalyst. The unreacted slurry of $CoCO_3.Co(OH)_2$ was separated from catalyst particles by 5-time decantation with distilled water and the samples were dried in a rotary vacuum evaporator at 95 °C for 1 h, sulphided, and labelled CoMo(WAS_{ox}).

Recently, spreading of the cobalt hydroxide carbonate over supported sulphidic Mo (WAS_{sulph}) was performed. The sulphided supported Mo catalyst was immersed into distilled water and $CoCO_3.Co(OH)_2$ was added. The nominal amount of 0.1 g of $CoCO_3.Co(OH)_2$ was used per 1 g of sulphided Mo catalyst. The mixture was heated under reflux condenser at 95 °C for 24 h. During the heating, the mixture was bubbled with air to increase partial re-oxidation of MoS_2 surface. This partial re-oxidation decreases PZC of sulphided Mo catalysts and increases sorption of Co. The

aspects of partial re-oxidation and sorption of Co are discussed above in Section 2.1. At the end, the unreacted slurry of $CoCO_3.Co(OH)_2$ was separated from catalyst particles by 5-time decantation with distilled water. The samples were dried in rotary vacuum evaporator at 95 °C for 1 h, sulphided and labelled as CoMo(WAS_{sulph}).

3.1.3. WAS_{sulph} over Extrudates

The original extrudates of the support were used for selected experiments instead of grain fraction. The extrudates were coded Al-262-e, Ti-140-e, and Zr-108-e. First, MoO_3 was deposited as it was described above. SEM-EDX measurements confirmed saturated and homogeneous profile of Mo concentration through the body of bisected extrudates. Saturated loadings of Mo were the same as it is shown in Table 2 for the catalysts prepared from grain fraction of the supports. Then, the extrudates were sulphided as it was described above and immersed into an aqueous slurry of $CoCO_3.Co(OH)_2$ under nitrogen. The mixture was left standing without any stirring for 14 days. After 14 days, the mixture was heated and stirred by bubbling air as described above. PZC and SEM-EDX measurements were done at various stages of the experiment. The samples of the extrudates were taken from the impregnation slurry, washed and dried as described above. These samples were bisected and analyzed by SEM-EDX for Co content.

3.2. Reference Catalyst

The industrial $CoMo/Al_2O_3$ (Albemarle, KF 756, Amsterdam, the Netherlands, 2.5 wt% Co, 12.2 wt% Mo, S_{BET} (sulphidic state) = 211 m^2g^{-1}) catalyst was used as reference catalyst in HDS of 1–benzothiophene.

3.3. Characterization

The point of zero charge (PZC) was measured by simplified mass titration method [40] with a WTW pH meter equipped with a cell Hamilton Slimtrode. The textural properties of the supports and selected sulphided catalysts were investigated by N_2 adsorption with a Micromeritics ASAP 2010 apparatus (Norcross, USA) after evacuation at 350 °C for 4 h. To calculate the specific surface area (S_{BET}), the data were treated by the standard BET method.

SEM-EDX was performed on a Tescan Indusem apparatus equipped with EDS (SDD XFlash® 5010, Bruker, Karlsruhe, Germany, resolution 125 eV), working at acceleration of 15 kV. Concentration profile was obtained by ten measurements equidistantly distributed from the center of the extrudate to the surface. Each measurement was acquired from squared area 60 × 60 um.

Temperature programmed reduction (H_2-TPR) was performed in the flow of H_2:Ar (1:19) with a temperature ramp 5 °C min^{-1} from 40 to 960 °C on a Micromeritics chemisorber AutoChem 2950 HP equipped with a thermal conductivity detector. The catalyst was placed in a quartz ampule and it was ex situ sulphided (details of the sulphidation are given above). The ampule was then filled with nitrogen and transferred into TPR apparatus. Selected samples were also allowed to be re-oxidized in laboratory environment for the selected time before the TPR experiments.

The superficial elemental analyses of the sulphidic catalysts were carried out on XPS (X-ray Photoelectron Spectrometer) spectrometer ESCA 3400 (Kratos, Manchester, Great Britain) with a base pressure in the analysis chamber of~$5.0 \cdot 10^{-7}$ Pa. The spectra were excited with an Mg Kα radiation ($h\nu$ = 1253.6 eV) generated at 12 kV and 10 mA. The selected samples were allowed to be re-oxidized in laboratory environment for selected time before the XPS experiments. Examples of comprehensive characterization of similar CoMo phases by XPS and by transmission electron microscopy (TEM) assessing the intrinsic activity of active sites can be found elsewhere in the literature [4,38,41,42].

3.4. Catalytic Activity

Hydrodesulphurization of 1–benzothiophene (BT) was performed in the gas phase using an integral fixed–bed tubular flow microreactor (i.d. 3 mm) at 360 °C and 1.6 MPa. Prior to the

measurements, the catalysts were sulphided in situ with an H_2S/H_2 flow (1/10) at 400 °C and atmospheric pressure with a temperature ramp of 10 °C min^{-1} and a dwell time of 1 h. The composition of the feed was kept constant at 16 kPa, 200 kPa and 1384 kPa of 1-benzothiophene (BT), decane and hydrogen, respectively. The catalyst sample (0.03–0.20 g) was diluted with an inert α–Al_2O_3 with particle size fraction 0.16–0.32 mm to form a bed length of 30 mm. The reaction was run at three feed rates of BT including 7.7 mmol h^{-1}, 10.3 mmol h^{-1} and 15.5 mmol h^{-1}. The steady state was reached in 30 min after each change in the feed rate. No changes of conversions during the following 1 h were observed. The reaction mixture was analyzed on a Hewlett–Packard gas chromatograph (6890 series, Waldbronn, 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 scheme of BT HDS is shown in Figure 5. The relative compositions a_{BT}, a_{EB} and a_{DH}, BT conversion x_{BT} and EB and DH yields, y_{EB}, and y_{DH} were defined as $a_{BT} = (1 - x_{BT}) = n_{BT}/n^0_{BT}$, $a_{EB} = y_{EB} = n_{EB}/n^0_{BT}$, $a_{DH} = y_{DH} = n_{DH}/n^0_{BT}$, where n^0_{BT}, n_{BT}, n_{EB}, and n_{DH} were the initial number of moles of BT, final number of moles of BT, EB, and DH, respectively. The rate constant of EB formation, k_{EB}, was calculated using an empirical pseudo-first-order rate equation ($a_{EB} = 1 - \exp(-k_{EB}W/F)$. An example of how relative composition depends on space time W/F and how k_{EB} was obtained is given in Figure 6.

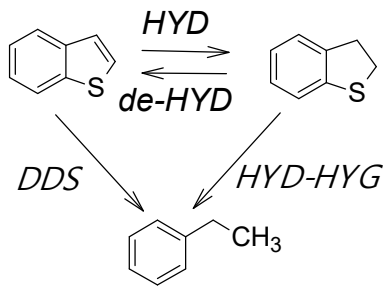

Figure 5. Scheme of 1-benzothiophene hydrodesulphurization: (HYD) hydrogenation of benzothiophene to dihydrobenzothiophene, (de-HYD) dehydrogenation of dihydrobenzothiophene to 1-benzothiophene, (HYD-HYG) hydrogenolysis of dihydrobenzothiophene to ethylbenzene (hydrogenation route), (DDS) hydrogenolysis of 1-benzothiophene to ethylbenzene (direct desulphurization route).

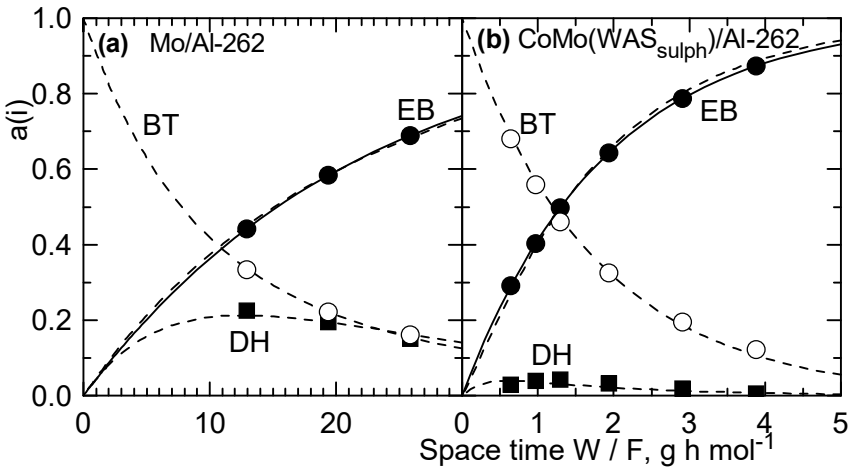

Figure 6. Relative composition during reaction of 1-benzothiophene (BT, open circles) hydrodesulphurization over Mo (**a**) and CoMo(WAS_{sulph})/Al-262 (**b**) catalysts: (DH, solid squares) dihydrobenzothiophene, (EB, solid circles) ethylbenzene, (dash lines) the curves calculated using the parallel consecutive scheme of four pseudo-first-order rate reactions from Figure 5, (solid line) the curve calculated using an empirical pseudo-first-order rate equation (see text) to determine empiric HDS activity k_{EB}.

4. Conclusions

Recently, the feasibility of the water-assisted spreading of the low solubility $CoCO_3.Co(OH)_2$ onto pre-sulphided Mo species was reported. Partial re-oxidation of sulphidic molybdenum during spreading decreased point of zero charge of molybdenum sulphide catalyst to 4, which allowed sorption of dissolved Co^{2+} cations from $CoCO_3.Co(OH)_2/H_2O$ slurry of pH of 8.5. The saturated adsorption loadings were higher than it was the case of Co spreading onto oxidic MoO_3/Al_2O_3, MoO_3/ZrO_2, and MoO_3/TiO_2 precursors. Systematic increase (16–86%) of HDS activity was observed after promotion of pre-sulphided and partially re-oxidized species of Mo in comparison to the promotion of oxidic Mo species. This new method thus led to more efficient promotion of HDS activity.

Furthermore, the spreading of $CoCO_3.Co(OH)_2$ onto the sulphided and partially re-oxidized Mo lead to an increase of reducibility of the deposited CoMo phase during temperature programed reduction. This was manifested by decreased temperature of the first reduction peak and increased reduction at temperatures above 300 °C, in comparison to the water-assisted spreading of $CoCO_3.Co(OH)_2$ and conventional deposition of Co nitrate onto MoO_3 catalysts. Promotional effects of Co deposited onto sulphided Mo phase in activity of benzothiophene HDS were 1.5–3.0 times higher than the promotional effects achieved by conventional impregnation and 1.1–1.9 times higher than the promotional effects achieved by water-assisted spreading onto the oxide Mo phase. The water-assisted spreading method does not principally need using nitrate or ammonium salts during synthesis. The catalysts in their dried stage can be directly sulphided without calcination. All these represent implications attractive for further research and industrial practice.

Supplementary Materials: The supplementary materials contain: 1. Additional information on re-oxidation of supported Mo sulphides in Figure S1: Raman spectroscopy of reaction of Mo/Al-262 with $CoCO_3.Co(OH)_2/H_2O$ slurry: bottom line–0 min (dried sulphided Mo/Al-262), upper line–example of patterns achieved between 1h–14 days of the WAS_{sulph} reaction at 25 °C or between 1 h–24 h of the WAS_{sulph} reaction at 95 °C and Figure S2: Re-oxidation of sulphided Mo/Zr-108 (**a**) and Mo/Ti-140 (**b**) followed by H_2-TPR; 2. Sorption of Co on sulphided Mo supported on Zr-108-e and Ti-140-e by SEM-EDX in Figure S3: Saturation of Mo/Zr-108-e (**a**) and Mo/Ti-140-e (**b**) by $CoCO_3.Co(OH)_2/H_2O$ slurry; 3. H_2-TPR of sulphided MoO_3, $CoCO_3.Co(OH)_2$ and the reference CoMo catalyst in Figure S4: H_2-TPR patterns of sulphided individual starting compounds and the reference commercial CoMo catalyst; 4. XPS surface analysis of selected sulphided catalysts in Figure S5. XPS Co $2p_{3/2}$ (**a**), Mo $3d_{5/2}$ (**b**), and S $2p_{3/2}$ (**c**) spectra. Binding energies (BE): (**a**) dot line–oxidic Co^{2+} (781.6 ± 0.5 eV), dash line–sulphidic Co^{2+} (778.3 ± 0.5 eV); (**b**) dot line–oxidic Mo^{6+} (232.0 ± 0.5 eV), dash dot line–MoS_xO_y (229.8 ± 0.5 eV), dash line–sulphidic Mo^{4+} (228.7 ± 0.5 eV), grey solid line–sulphur S 2s; (**c**) dot line–sulphates SO_4^{2-} (169.5 ± 0.5 eV), dash line–sulphides S^{2-} (162.4 ± 0.5 eV); and 5. Selectivity to dihydrobenzothiophene (DH) during 1-benzothiophene (BT) HDS in Figure S6. Selectivity to dihydrobenzothiophene (DH) during 1-benzothiophene (BT) HDS: crossed squares–CoMo(CIM_{ox}), open squares–CoMo(WAS_{ox}), and solid squares–CoMo(WAS_{sulph}).

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