

Research Article

Highly Active Low Cobalt Content-Based Bulk MoS₂ Hydrodesulfurization Catalysts with a Unique Impact of H₂S

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A series of unsupported MoS₂, Co₉S₈, and Co-promoted MoS₂ catalysts have been synthesized by tuned impregnation and successive thermal annealing methods using a continuous flow of a mixture of H₂ and H₂S gases. The resulting catalysts were evaluated in terms of their activity and selectivity for the hydrodesulfurization of dibenzothiophene (DBT) both in the absence and the presence of H₂S. The inclusion of Co onto MoS₂ affected both the hydrogenation and direct desulfurization reactions, with the latter (production of biphenyl) being magnified to a much greater degree than the former. Interestingly, low cobalt/molybdenum ratio of ca. 0.05 of the catalyst exhibited outstanding promotion efficiency in the hydrodesulfurization reaction. However, as cobalt is added, the synergy effect drastically decreased. H₂S in the reaction mixture led to a remarkable step up in the product from the direct desulfurization reaction route with the most notable increases occurring for the product from the hydrogenation reaction pathway. The HDS activity of such catalysts was much higher than that of the commercial CoMo/Al₂O₃. The promotion by H₂S was discussed.

1. Introduction

Significant research efforts have been directed towards the development of catalysts for better reducing the sulfur contents of petroleum fuel fractions [1–4]. Dwindling oil supplies, especially those extracted under vacuum distillation, and recent stringent environmental regulations aimed at limiting the sulfur contents of transportation fuels have resulted in a strong demand for improved hydrothermal treatment techniques. Clean fuels, such as sulfur- and nitrogen-free fuels, not only have the advantage of being environmentally benign transportation fuels but can also be used in several other emerging energy-related fields, including fuel cells [5]. The main catalysts used in hydrothermal treatment processes are Ni- and/or Co-containing

Mo-based Al₂O₃ catalysts. Such catalysts are proved to be highly active for thiophenes and benzothiophenes sulfur elimination. However, they are not sufficiently active for desulfurizing compounds such as dibenzothiophene (DBT), and it is analogous. This is particularly problematic because these compounds are the major sulfur-containing species remaining in the middle distillate fractions and in the atmospheric or heavy residues. The MoS₂ phases are the main catalysts in hydrothermal treatment reactions such as hydrodesulfurization (HDS). The addition of Co to supported MoS₂ catalysts has been studied intensively, and its role as a promoter in HDS reactions is well established. MoS₂-based catalysts with no promoter have very low activities towards HDS reactions. The significant enhancement in the HDS performance of these catalysts following the

incorporation of Co has been attributed to the synergy between the Co and Mo phases [6–9]. The details of this synergy have been investigated extensively in previous occasions [10–12]. However, the influence of the incorporation of Co on the selectivity of such MoS₂-based catalysts towards the HDS reactions is far from being fully understood [13–17]. The nature of the interactions between the Mo support and the substrate can have a significant impact on the efficiency of the synergy caused by Co and/or Ni promoters. On the contrary, the function of the promoter in the bulk MoS₂ in the HDS reaction remains beyond a complete coverage. Catalysts of this type have high activities in HDS reactions [18]. Although a large number of reports are available for CoMo-based catalysts, relatively very little information has been published pertaining to the unsupported CoMo catalysts. A better understanding of how Co or Mo modifies the activity of bulk MoS₂ or Co₉S₈ catalysts could provide valuable information for the development of new Mo-based catalysts for hydrothermal treatment processes. In this study, the DBT HDS reactions using bulk MoS₂, Mo-Co₉S₈, and Co-MoS₂ catalysts containing various amounts of Co, especially in low cobalt concentration range, were investigated. The potential of Co as a promoter of the bulk MoS₂ catalyst is dealt with. The effects of the hydrogen sulfide matrix on the catalytic performance of the HDS reaction of DBT were also evaluated.

2. Experimental

2.1. Materials and Methods. Cobalt acetate tetrahydrate [Co(C₂H₃O₂)₂·4H₂O], ammonium heptamolybdate tetrahydrate [(NH₄)₆Mo₇O₂₄·4H₂O] (AH), ammonium tetrathiomolybdate [NH₄]₂[MoS₄] (AT), molybdenum acetylacetonate [C₁₀H₁₄MoO₆], DBT, and decane were supplied from Wako Chemical Industries, Ltd. All chemicals were exploited as received. The bulk MoS₂ catalysts, AHS and ATS, were prepared by heat annealing the corresponding Mo precursors (AH and AT) in the presence of a concurrent flow of a 1:9 (v/v) mixture of H₂S/H₂ gas at 830°C and 400°C, respectively. Co₉S₈ (CS) was also synthesized from the heat annealing of Co-acetate tetrahydrate at 400°C following the same procedure as before. The details of such processes have been described elsewhere [19]. A sample of the AHS material (obtained by sulfiding the ammonium heptamolybdate tetrahydrate precursor) was comminuted using a mill with an inner volume of 100 mL equipped with a media of zirconia beads, which was purged with He prior to being used. The resulting material was denoted as AHS-G. The BET surface areas of AHS, AHS-G, and ATS, which were measured using automatic Micromeritics ASAP 2010 instrument by N₂ adsorption-desorption technique at -196°C, were approximately >10, 115, and 65 m²/g, respectively. The AHS-G and ATS sulfide samples were used as preliminary supports for the addition of the Co precursor. The Mo-sulfide phase was impregnated with a 1:1 (v/v) mixture of water/alcohol containing a specific amount of cobalt acetate tetrahydrate at an ambient temperature. The solution was then subjected to sonication for 3 h, followed by drying in air and thereafter

heating in a vacuum oven at 120°C overnight. All catalysts were thereafter subjected to sulfidation with a stream of a 1:9 (v/v) mixture of H₂S/H₂ gases (5 ml/min) at 400°C. The resulting samples were denoted as C-AHSG- and C-ATS-, I to III based on their Co loading. Another sample was synthesized in which the prepared Co₉S₈ phase was impregnated with a certain amount of an alcoholic solution of molybdenum acetylacetonate following the typical procedure mentioned before until obtaining the sulfide form of the catalyst. This sample (denoted as MPC) represents the Mo-promoted cobalt sulfide catalyst of ca. 0.4 of the Co/(Co + Mo) atomic ratio. The commercial CoMo/Al₂O₃ catalyst was also studied for comparison. All Mo-sulfide samples exhibited a hexagonal molybdenite-2H structure (JCPDS# 65-0160) according to the XRD patterns of AHS, AHS-G, and ATS catalysts shown in Figure 1, which is in agreement with literature [20].

No phases other than MoS₂ were detected. On the contrary, the diffraction patterns of the synthesized Co-sulfide phase matched well with the JCPDS# 73-1442 of Co₉S₈. The AHS-G and ATS catalysts had MoS₂ crystallite sizes of approximately ≈5 nm. Transmission electron microscopy images (obtained from TEM; JEOL-2000EX) for C-ATS-I were depicted in Figure 2. Five to 10 layers of MoS₂ is obviously noted. Interlayer spacing of ca. 0.62 nm was determined from the (002) XRD peak at 2θ of 14.2.

2.2. Activity Measurements. The catalysts were investigated for the DBT HDS reaction. DBT was selected as a model compound for these reactions because it is a representative of some of the sulfur-containing refractory compounds found in middle distillates and heavy residue. All tests were implemented under a 3 MPa of H₂ pressure and at 340°C. The experiments were conducted using a stainless steel batch microautoclave reactor (100 mL) equipped with a magnetic stirrer and stainless steel filter, which allowed convenient withdrawal of small samples from the reaction mixtures at regular time intervals. A decane solution of DBT (1 wt.%) was used as the reaction feedstock. Some reaction runs were conducted in the presence of Cu powder (ca. 0.7 g), which was used as a scrubber for the H₂S produced as a by-product during the HDS reaction. A blank run was also conducted with Cu in the absence of a catalyst, which confirmed that Cu did not exhibit any activity towards the DBT HDS reaction. The effect of the reaction matrix was evaluated by investigating the reaction over the present catalysts in both with and without the existence of H₂S in the feedstocks. Immediately before the reaction test, the catalyst was once more subjected to a sulfidation step with a mixture of H₂S/H₂ gases. The catalyst and the reaction mixture (a typical of 15 mL of 1 wt.% DBT in decane) were loaded in situ into the reactor, which was subsequently pressurized with H₂ and heated to 340°C under continuous stirring at 1000 rpm. Small samples of the reaction mixture (0.1–0.2 mL) were withdrawn from the reactor periodically for analysis to determine the rate of conversion. Gas chromatography (Agilent HP 6890) and GC-mass spectrometry (GC-MS) equipped with an Agilent HP 5970 MS were used

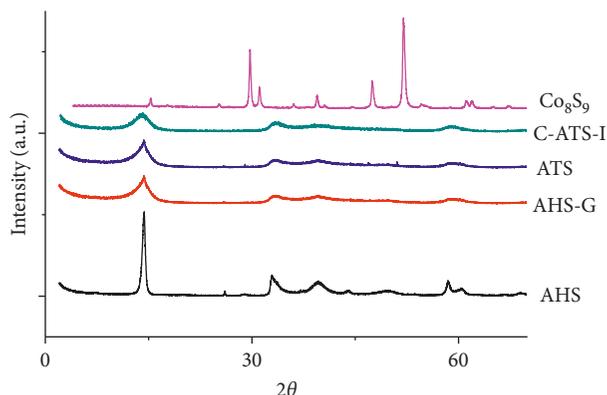


FIGURE 1: XRD patterns of the AHS, AHS-G, ATS, C-ATS-I, and Co_9S_8 catalysts.

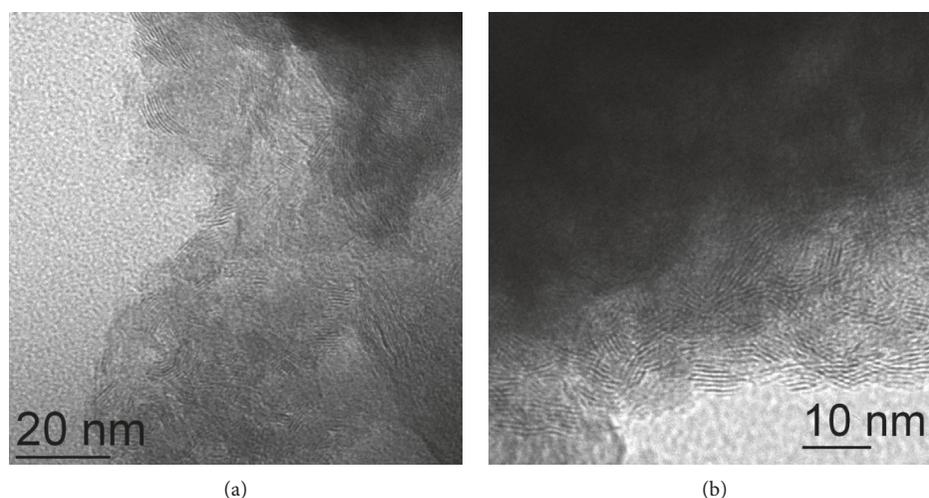


FIGURE 2: TEM images of the C-ATS-I catalyst.

to analyze the reactions. All GC analyses were conducted on a methylsiloxane capillary column (0.32 mm \times 50 m).

3. Results and Discussion

3.1. Catalyst Performances. The main HDS reaction products obtained under the operating terms described above over the present catalysts were cyclohexylbenzene (CB), biphenyl (BP), 1,2,3,4-tetrahydrodibenzothiophene (H4-DBT), and H_2S . Trace quantities of the different isomers of partially hydrogenated DBT were also detected. Based on these products, we have proposed two reaction pathways for DBT HDS, which are depicted in Scheme 1.

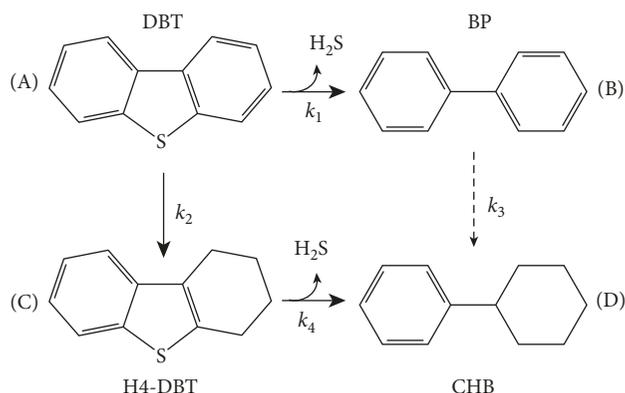
The rate constants for these transformations were estimated by fitting the experimental data using a nonlinear least square analysis on the supposition that the HDS reaction behaves kinetically as pseudo-first-order [3, 4, 8, 9]. Figure 3 shows the fit curves for the DBT HDS over the C-ATS-I catalyst under different levels of H_2S .

The reaction system was classified into two reaction routes, including (1) hydrogenation (HYD), which would

involve the initial formation of H4-DBT and its isomers by partial hydrogenation of DBT, followed by further reduction of these intermediates to give CB and (2) direct desulfurization (DDS), which would produce BP directly by the C-S bond scission. These data were treated kinetically and evaluated according to the model that was recently developed for consecutive-parallel reactions [21]. Based on this approach, we used the following differential equations to calculate the catalytic constants:

$$\begin{aligned} C_A &= C_{A^0} \exp^{-k_0 t}, \\ C_B &= \frac{C_{A^0} k_1^0}{k_3^0 - k_0} \left[\exp^{-k_0 t} - \exp^{-k_3^0 t} \right], \\ C_C &= \frac{C_{A^0} k_2^0}{k_4^0 - k_0} \left[\exp^{-k_0 t} - \exp^{-k_4^0 t} \right], \end{aligned} \quad (1)$$

where $k_0 = k_1 K_1 + k_2 K_2$ and k_1 and k_2 denote the DDS and the HYD intrinsic kinetic rate constants, respectively. K_1 and K_2 point to the constants of DBT adsorption at equilibrium onto the DDS and HYD reaction sites, respectively.



SCHEME 1: Reaction scheme for HDS of dibenzothiophene.

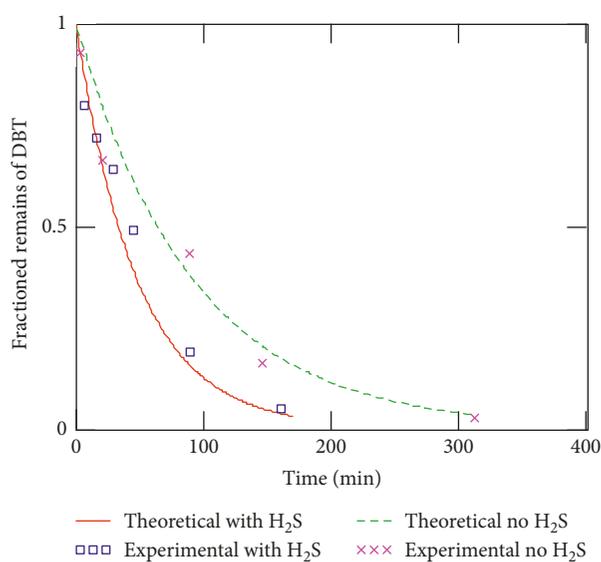


FIGURE 3: Pseudo-first-order plots for the HDS reactions of DBT over the C-ATS-I catalyst in the absence and presence of H₂S.

The kinetic parameters were adjusted for each compound according to the following formula: $k_n^0 = k_n K_n$, where K_n and k_n are the equilibrium adsorption and intrinsic kinetic rate constants of each compound, respectively. This treatment provided a better estimation of the individual contributions of the hydrogenation and direct desulfurization reaction pathways to the HDS reaction. Furthermore, this process allowed more reliable quantification of the individual reaction rates according to the contribution of each reaction pathway. The experimental data were solved and fitted to the model using the Mathcad program. The estimated activity data are listed in Table 1.

Figures 4 and 5 show the nonlinear curves that were fitted with the product yields from the HDS reaction over the C-ATS-1 catalyst in the presence and in the absence of H₂S, respectively, using the model described above. All catalysts tested in this study provided a reasonable fit to the data exposed from the HDS reaction. The C-ATS-I catalyst displayed much higher level of reaction activity than the ATS, AHS-G, C-AHS-G, MPC, and commercial

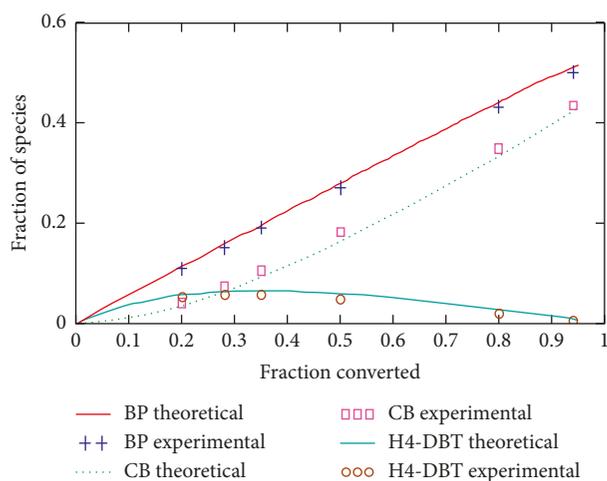
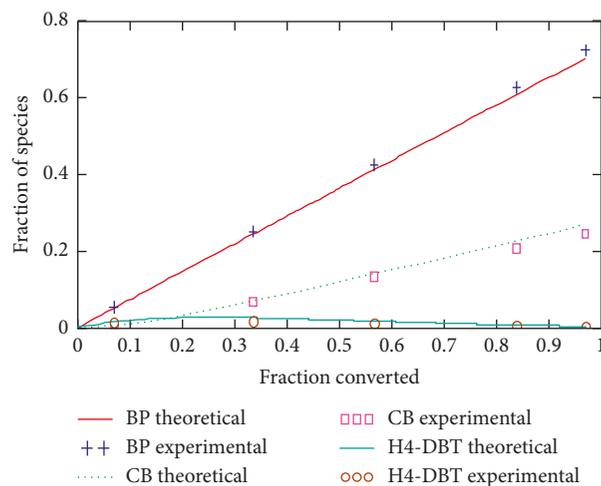
CoMo/Al₂O₃ catalysts. However, DBT HDS proceeded to a lower activity over the C-AHS-G catalysts than it did over the bare commuted MoS₂ catalyst. The difference in the activity of these two systems could be attributed to the delicate structure of the commuted MoS₂ as a primary support, which led to differences in the specific surface areas of these catalysts (the surface area (BET) of the AHS-G catalyst was 110 m²/g, and therefore, it is much higher than that of the C-AHS-G-II catalyst, which was less than 5 m²/g). Thus, commuted MoS₂ may not be a recommended preliminary support for Co promotion. Taken together, these results indicate that the selectivity profiles of the catalysts need to be analyzed in a greater detail to develop a better view of the changes in the activity following the impregnation of the catalysts with Co. In this study, the selectivity was estimated according to the determined ratio of the HYD to the DDS rate constant, that is, $k_{\text{HYD}}/k_{\text{DDS}}$. One should be careful when considering the catalytic selectivity according to the product distributions because the selectivity in this case underwent significant mobile changes depending on the level of conversion (Figure 4). When the bare MoS₂ catalysts were used, the HDS of DBT proceeded preferentially by the HYD route, as shown in Table 1. The relatively high selectivity observed in this case for the products resulting from the HYD route is contrary to the common view that DBT HDS proceeds mostly by a DDS route. These results therefore highlight the flexibility of the HDS reaction, in the sense that it can proceed by these routes with no path limitation to either of them.

The impregnation of Co onto the ATS catalyst (C-ATS series of catalysts) led to a significant development in the overall HDS activity. One may notice the obvious pioneer Co promotion in the HDS of these catalysts, especially for the C-ATS-I catalyst. This catalyst showed a remarkable tendency towards the DDS pathway (ca. 1~2-fold higher activity towards the DDS route over the HYD route (Table 1)) for the HDS of DBT, whilst the bare MoS₂ catalysts exhibited a preference for the HYD pathway. The change in the activity of the Co-containing catalyst was accompanied by an obvious shift in its selectivity towards the BP product. This tendency towards the DDS pathway has been reported previously for the conventional MoS₂-based catalysts as a result of the impregnation of a Co promoter [5]. These results therefore demonstrate that the HYD and DDS reaction pathways occur in parallel and can be independently manipulated. Notably, all Co catalysts prepared in this study underwent the HDS reaction preferentially by the DDS pathway, and a clear correlation between the selectivity and activity of the HDS reactions could be established (Figure 6(a)). It is noteworthy mentioning that the trend in the selectivity of these reactions was in accordance with similar reports from the literature for related systems [3]. Figure 6(b) displays the association between the reaction activity of the C-ATS catalysts and the Co/(Co + Mo) ratio. It is obvious that the C-ATS-I catalyst, which had 0.05 Co/(Co + Mo) ratio, exhibited the highest HDS activity of all of the catalysts belonging to this series. Interestingly, such ratio is far lower than those commonly reported for conventional Co-Mo-based catalysts, where the average is

TABLE 1: Activities of the catalysts towards the HDS of dibenzothiophene.

Catalyst	Co/(Co + Mo) atomic ratio	Level of H ₂ S ^a	HDS activity (sec ⁻¹ g.cat. ⁻¹ · 10 ⁻⁴)	Individual activity (sec ⁻¹ g.cat. ⁻¹ · 10 ⁻⁴)			Products at 50% conversion level		
				k ₁ ^b	k ₂ ^c	k ₂ /k ₁	BP	CB	H4-DBT
AHS-G	—	L	24	10	14	1.4	23	25	2
		H	77	15	62	4.0	8	29	13
ATS	—	L	9	3.9	4.8	1.2	23	24	3
		H	38	6.7	31.4	4.7	8	28	14
CoMo/Al ₂ O ₃ ^e	0.27	L	211 ^d	191	20	0.1	46	3	1
		H	128 ^d	112	16	0.14	43	6	1
C-AHSG-I	0.02	H	38	21	17	0.8	29	16	5
C-AHSG-II	0.23	L	17	14	3	0.2	43	6	1
		H	33	20	13	0.7	28	17	5
C-ATS-I	0.05	L	184	127	57	0.4	37	12	1
		H	352	194	158	0.8	27	18	5
MPC	0.40	L	1.8 ^f	1.6	0.2	0.12	43	6	1
		H	2.6 ^f	1.8	0.8	0.4	37	12	1
CS	—	L	1.6 ^f	0.8	0.8	1	24	22	4
		H	1.6 ^f	0.8	0.8	1	24	22	4

^aLevel of H₂S: low (L) and high (H) denote pressures of ca. 3 and 20 kPa, respectively. ^bApparent rate constant for the direct desulfurization route, 1st order. ^cApparent rate constant for the hydrogenation route, 1st order. ^dNormalized to the metal sulfide content. ^eCommercial catalyst Co, 3.2%, and Mo, 13.7%, in terms of the weight percent. ^fPseudo-zero-order rate constant, × 10¹⁷ molecule/(g·S). The uncertainty was within ±5–10%.

FIGURE 4: Transformation of dibenzothiophene over the C-ATS-I catalyst in the presence of H₂S.FIGURE 5: Transformation of dibenzothiophene over the C-ATS-I catalyst in the absence of H₂S.

generally around 0.3. However, the present results are generally in a trend with other studies where low Co concentration catalysts were reported to be active for hydrogenation and hydrogenolysis reactions [22, 23]. The selectivity for the HYD reaction was clearly effected by the amount of Co incorporated into the existing catalyst. The results in Figure 6(b) show that the tendency towards the HYD reaction decreased with the increase in Co content. These results therefore may indicate that only a limited number of active Mo and S sites can be further activated by the inclusion of Co. These sites were assumed to be in the type II CoMoS phase.

The active sites of HDS catalysts are coordinately unsaturated sites. The incorporation of promoters such as Co and Ni can lead to improvements in the supply of spillover hydrogen. This may lead to an increase in the DDS and HYD activities [9, 12, 15, 16, 21]. It is therefore envisaged that

these catalysts must contain different types of active sites to allow them to catalyze multiple reactions in parallel. The Co atoms incorporated into the MoS₂ catalysts could occupy the active sites on their surface. The enlargement in the catalytic activity of the Co-containing MoS₂ catalysts (i.e., C-ATS catalysts) compared with the bare MoS₂ catalyst could be attributed to the occurrence of a large synergistic effect (Table 2) between Co and Mo atoms. A synergistic effect of this type could potentially result in the formation of two different Co-based active sites for the DDS and HYD reactions. The Co atoms could therefore occupy different positions on the surface (i.e., edges and corners) of the unsaturated MoS₂ sites, resulting in new sites. However, not all of these sites would be accessible for the HDS reaction of the substrate. The results therefore imply that the higher activity of these compounds could be attributed to an increase in the effectiveness of the active sites. The corner-edge

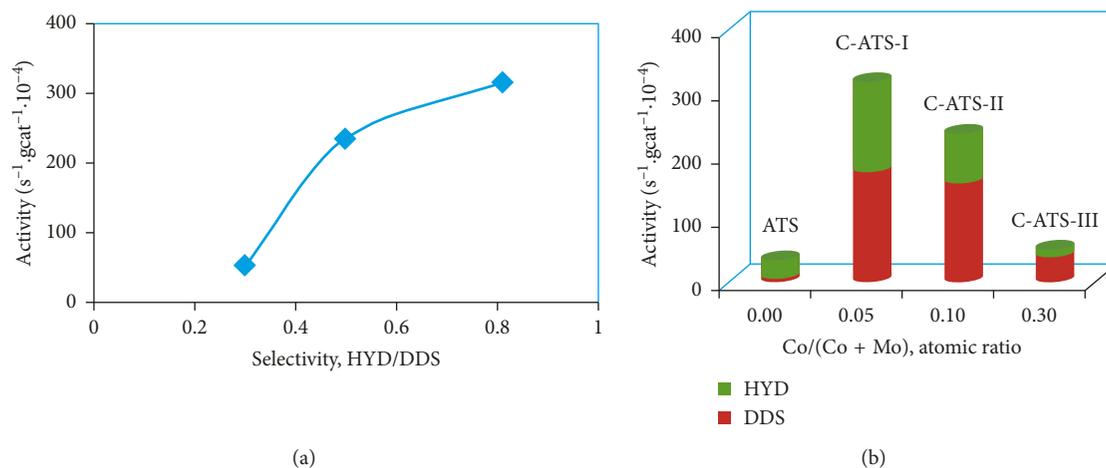


FIGURE 6: Effect of the Co content on the HDS activity (a) and the relationship between the activity and the selectivity (b).

TABLE 2: Changes in the selectivity of the HDS reaction for the MoS_2 -based catalysts caused by Co and H_2S .

Comparison of the average fold change (increase or decreases) in the activity of the ATS catalyst due to the inclusion of Co						
Reaction condition		Absence of H_2S			Presence of H_2S	
Catalyst		C-ATS-I			C-ATS-I	
DBT	DDS	+33			+29	
	HYD	+12			+5	
Comparison of the average fold change (increase or decrease) in the activity caused by H_2S						
Catalyst		C-AHSG-II	AHS-G	C-ATS-I	ATS	CoMo/ Al_2O_3
DBT	DDS	+1.4	+1.5	+1.5	+1.7	-1.7
	HYD	+4.3	+4.4	+2.8	+6.5	-1.3

+, increase; -, decrease.

model [24–26] can be used to explain the differences in the selectivity profiles of promoted and unpromoted MoS_2 catalysts for the DDS route. The Mo atoms at the corner sites of the stacked cluster would probably be unsaturated because of the steric configuration of the hexagonal crystals in the catalyst. There could also be a high proportion of coordinately unsaturated sites in this case. It can be concluded that the selectivity of the catalysts for the DDS reaction correlates highly with the number of MoS_2 layers. Nikulshin et al. [27, 28] in studies for the HDS over CoMo-based catalysts showed that the (Co/Mo) edge ratio is directly proportional with the catalyst HDS activity. They further revealed that, with increasing the cobalt content, the HDS selectivity turns slightly towards HYD but still the predominant route is the DDS. To date, our preliminary results have shown that the low content of the Co-promoted MoS_2 catalyst, especially the C-ATS catalysts, and led to an increase in the overall activity. On the contrary, MPC catalyst exhibited low HDS performance. Furthermore, the reaction followed pseudo-zero-order kinetics (Figures S1–S3).

3.2. Impact of H_2S . The H_2S matrix could also have a significant impact on the behaviors of the catalysts developed in this study for the HDS reaction. The activities and selectivities of the current catalysts towards DBT HDS varied considerably depending on the existence of H_2S in the reaction medium. The parameters derived from the kinetic

treatments of these experimental results are presented in Table 1. Several clear and interesting trends can be observed. For example, the presence of H_2S resulted in a slight rise in the formation of BP (DDS route product). However, the inclusion of H_2S also drove to a remarkable positive change in the tendency of the reaction towards the HYD route and the production of CB. Table 2 shows that the presence of H_2S led to a rise in the activity of the present catalysts by increasing the rates of the HYD and DDS reactions by approximately 2.5- to 4-fold and 1.4- to 1.7-fold, respectively. The promotional trends of H_2S towards the DDS reaction were very similar for all of the prepared catalysts. For instance, the enhancement in the activity resulting from the inclusion of H_2S was much more pronounced for the HYD reaction route, especially in case of the bare MoS_2 catalyst. The HYD pathway contributed to more than 80% of DBT HDS over AHS-G and/or ATS catalysts. H_2S influence on the HDS reaction has been discussed extensively in various studies [29–35], which consensually suggested that H_2S suppresses the DDS route, whilst having very little impact on the HYD route. In contrast, several research groups, including our own, have reported that some transition metal sulfide catalysts can effectively promote the HYD reaction when they are carried out in the presence of H_2S [36–38]. Guernalec et al. [38] correlated this positive behavior to the increase of the -SH concentration on the catalyst surface. However, our obtained results represent a unique catalytic

trend in which the use of H_2S may promote the HDS reaction over unsupported Co-promoted MoS_2 catalysts. The increase observed in the catalytic activity in presence of H_2S reported here is contrary to the well-known observation that H_2S severely inhibits the HDS reactions that are conducted over conventional catalysts. This is evident from the data highlighting the inhibition of the commercial $\text{CoMo}/\text{Al}_2\text{O}_3$ catalyst by H_2S presented in Tables 1 and 2. Interestingly, this reaction (impacted by H_2S) was found to be reversible indicating that H_2S may have caused no permanent changes to the structure of the catalyst. Taken together, these results demonstrate that our collective understanding of H_2S influence on the selectivity of the HDS reaction is rather incomplete. Crystallite sizes in the extent of 4-5 nm for the MoS_2 crystallites appeared to exert a specific catalytic performance, which definitely depends on how such catalyst is synthesized. The nature of substrate, catalyst, and reaction conditions therefore appear to be of considerable importance for quantitative evaluation of this phenomenon.

3.3. Synergy Effect. The results of this study clearly show that the incorporation of Co had a decisive influence on the catalytic performance of the unsupported MoS_2 catalysts (series C-ATS). It is noteworthy mentioning that the results are consistent with the well-known promoting effects of conventional supported MoS_2 catalysts. Taken together, these results suggest that the HDS reaction resulted from divergent active sites. The synergy between the Co and Mo phases appeared to be on line with that claimed for the well-known Co-Mo-S type II materials, such as the supported Co-Mo catalysts [10], which are assumed to be responsible for catalyzing HDS reactions. All C-ATS catalysts prepared in the present study exhibited some degree of synergy between the Co and Mo atoms. This synergistic interaction enhanced the HDS reaction by promoting the DDS route to a higher extent than that of the HYD route. This result indicated that the Co-based sites were more effective for the C-S bond scission. Thus, it can be stated that the incorporation of Co not only improved the activity of the catalyst but also modified the selectivity along the two pathways. Figure 7 shows the relation between the synergy factor (SF, activity ratio of $(\text{Co-MoS}_2/\text{MoS}_2)$) and the Co-added ratio. Calculations based on the density functional theory (DFT) for such system have predicted that the sulfur and the metal edges of the catalyst may conduct the DDS reactions [34, 35]. These DFT studies have also shown that the Co atoms can be accommodated on the rims of the MoS_2 crystallites especially on the rims of the sulfur atoms.

It has been suggested that the HYD reactions most likely occur on the brim sites and the metal edges. In the present study, CB was isolated as the major product from the reactions catalyzed by the bare MoS_2 catalyst, which indicated that the HYD pathway was favored under these conditions. However, Table 1 shows that the share from the DDS route was higher than that of the HYD route when the HDS reaction was conducted over the C-ATS-I catalyst. The overall HDS activities of the ATS and C-ATS catalysts in the presence of H_2S were much higher than those in case of the

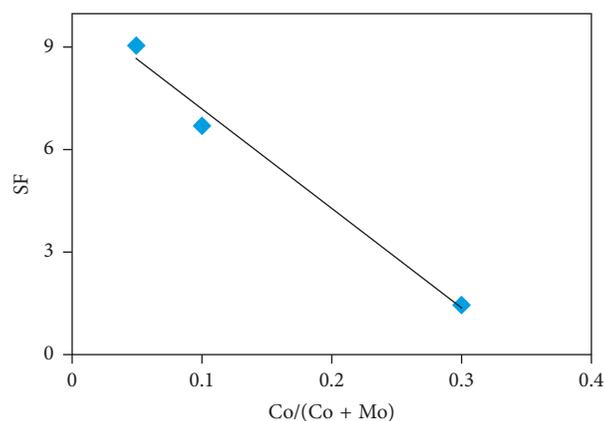


FIGURE 7: Cobalt content as a function of synergy promotion.

absence of H_2S . The major enhancement was in the HYD reactions of DBT. The MoS_2 and Co-containing MoS_2 catalysts contain acidic sites on their surfaces of two different types, including (i) Lewis acidic sites, that is, the sulfur vacancies on the Mo and Co atoms, and (ii) Bronsted acidic sites. The latter of these two sites would contain the -SH and -SH₂ groups. The -SH sites may act to eliminate sulfur from DBT and the HYD reactions (under certain circumstances), whilst the -SH₂ sites would favorably be involved in hydrogenation reactions. The involvement of these active sites in the HDS reaction would be dependent on their availability with the appropriate geometry to interact with the substrate [8, 35]. Given that the Co-S bond is relatively weaker than the Mo-S bond, the Co sites would be more acidic than the Mo sites [39]. This diversity in the acidity of the two sites could explain the higher DDS activity of the Co-containing MoS_2 catalysts compared with the unpromoted MoS_2 catalyst. The cleavage of the S-C bonds is most likely to occur with greater ease over the Co-promoted catalyst. This suggestion is also consistent with the results obtained for the commercial $\text{CoMo}/\text{Al}_2\text{O}_3$ catalyst (Table 1). It has therefore been suggested that the inclusion of H_2S may result in new active sites through interactions with vacant sulfur sites on the MoS_2 and Co-containing MoS_2 catalysts. The quality of these sites for promoting or suppressing the HYD and hydrogenolysis reactions would probably be dependent not only on their configuration and concentration but also on the structure of the substrate layers. The data shown in Table 2 provide a summary of the effects of Co and H_2S on the HDS reaction. The main points that could be drawn from the data are as follows:

- (1) The incorporation of Co (low concentration range) into the unsupported MoS_2 catalyst led to a significant activity boost in the DBT HDS reaction, as well as resistance to the inhibition phenomena caused by H_2S .
- (2) The Co atoms preferentially may occupy the edge sites of the MoS_2 catalyst [34, 35].
- (3) H_2S inclusion in the HDS reaction feedstock led to an enhancement in the hydrogenation activities of all the studied catalysts.

- (4) The incorporation of Co into the MoS₂ catalyst resulted in a drastic selectivity change towards the DDS reaction, which increased by an order of magnitude over the HYD reaction.
- (5) The presumable Co-SH₂ active sites may be much more effective for the HDS reaction than the Mo-SH₂ active sites.
- (6) Mo may, however slightly, promote the Co₉S₈ catalyst in the HDS reactions.

4. Conclusions

The catalytic results of the comminuted MoS₂, ATS, and Co-containing MoS₂ catalysts for the reaction of DBT showed that the nature of the preliminary MoS₂ support had a critical role on the activity of the Co-promoted one. The hydrogenation route was most predominant in the reaction over the bare MoS₂. H₂S inclusion enhanced the rates of both possible reaction routes but promoted the HYD pathway to a much greater extent. The activity of the MoS₂ catalysts increased significantly when the Co promoter was added. All catalysts synthesized in the current study exhibited a close trend towards the influence of H₂S in the HDS reaction. The C-ATS and C-AHSG catalysts showed a strong preference for the DDS pathways, with BP being produced as a major product. The boost in the activity observed with the Co-containing catalyst (C-ATS) was attributed to the obvious enhancement in the DDS route and to the significant increase in the HYD route reactions. The results from the kinetic analysis of the HDS reactions over the MoS₂ and MoS₂ promoted by Co catalysts suggested the existence of different discrete active sites, which were dependent on the identity of the promoter synergy and the reaction matrix. This study therefore provides important information for controlling the selectivity and activity characteristics of MoS₂-based catalysts by tailoring their properties through synthetic manipulation and promoter ratio and adapting proper reaction matrices.

Data Availability

The experimental data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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Supplementary Materials

Figure S1: pseudo-zero-order kinetics of HDS of DBT over the MPC catalyst in the presence or absence of H₂S. Figure S2: product distribution curves of DBT HDS over the MPC catalyst in the presence of H₂S at 340°C and 3 MPa H₂. Figure

S3: product distribution curves of DBT HDS over the MPC catalyst in the absence of H₂S at 340°C and 3 MPa H₂. (*Supplementary Materials*)

References

- [1] I. Mochida and K.-H. Choi, "An overview of hydrodesulfurization and hydrodenitrogenation," *Journal of the Japan Petroleum Institute*, vol. 47, no. 3, pp. 145–163, 2004.
- [2] D. D. Whitehurst, T. Isoda, and I. Mochida, "Present state of the art and future challenges in the hydrodesulfurization of polyaromatic sulfur compounds," *Advances in Catalysis*, vol. 42, pp. 345–471, 1998.
- [3] Z. Wu, V. M. L. Whiffen, W. Zhu, D. Wang, and K. J. Smith, "Effect of annealing temperature on co-MoS₂ nanosheets for hydrodesulfurization of dibenzothiophene," *Catalysis Letters*, vol. 144, no. 2, pp. 261–267, 2014.
- [4] J. Ancheyta-Juárez, E. Aguilar-Rodriguez, and D. Salazar-Sotelo, "Effect of hydrogen sulfide on the hydrotreating of middle distillates over Co-Mo/Al₂O₃ catalyst," *Applied Catalysis A: General*, vol. 183, no. 2, pp. 265–272, 1999.
- [5] C. Song, "An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel," *Catalysis Today*, vol. 86, no. 1-4, pp. 211–263, 2003.
- [6] M. L. Vrinat and L. D. Mourgues, "On the role of cobalt in sulfided unsupported Co-Mo hydrodesulfurization catalysts: kinetic studies and scanning electron microscopic observations," *Applied Catalysis*, vol. 5, no. 5, pp. 43–57, 1983.
- [7] G. Meijburg, *Production of Ultra Low-Sulfur Diesel in Hydrocracking with the Latest and Future Generation Catalysts Courier 46*, Akzo Nobel, Amsterdam, Netherlands, 2001.
- [8] M. Egorova and R. Prins, "Competitive hydrodesulfurization of 4,6-dimethyldibenzothiophene, hydrodenitrogenation of 2-methylpyridine, and hydrogenation of naphthalene over sulfided NiMo/γ-Al₂O₃," *Journal of Catalysis*, vol. 224, no. 2, pp. 278–287, 2004.
- [9] H. Topsøe, B. S. Clausen, and F. E. Massoth, *Hydrotreating Catalysis (Catalysis-science and Technology)*, Vol. 11, Springer, New York, NY, USA, 1996.
- [10] Z. Vít, D. Gulková, L. Kaluža, and M. Zdražil, "Synergetic effects of Pt and Ru added to Mo/AlO sulfide catalyst in simultaneous hydrodesulfurization of thiophene and hydrogenation of cyclohexene," *Journal of Catalysis*, vol. 232, no. 2, pp. 447–455, 2005.
- [11] E. J. M. Hensen, H. J. A. Brans, G. M. H. J. Lardinois, V. H. J. De Beer, J. A. R. Van Veen, and R. A. van Santen, "Periodic trends in hydrotreating catalysis: thiophene hydrodesulfurization over carbon-supported 4d transition metal sulfides," *Journal of Catalysis*, vol. 192, no. 1, pp. 98–107, 2000.
- [12] A. Ishihara, F. Dumeignil, J. Lee, K. Mitsushashi, E. W. Qian, and T. Kabe, "Hydrodesulfurization of sulfur-containing polyaromatic compounds in light gas oil using noble metal catalysts," *Applied Catalysis A: General*, vol. 289, no. 2, pp. 163–173, 2005.
- [13] M. Egorova and R. Prins, "Hydrodesulfurization of dibenzothiophene and 4,6-dimethyldibenzothiophene over sulfided NiMo/γ-Al₂O₃, CoMo/γ-Al₂O₃, and Mo/γ-Al₂O₃ catalysts," *Journal of Catalysis*, vol. 225, no. 2, pp. 417–427, 2004.
- [14] M. Kouzu, K. Uchida, Y. Kurili, and F. Ikazaki, "Microcrystalline molybdenum sulfide prepared by mechanical milling as an unsupported model catalyst for the hydrodesulfurization of diesel fuel," *Applied Catalysis A: General*, vol. 276, no. 1-2, pp. 241–249, 2004.

- [15] A. Niquille-Röthlisberger and R. Prins, "Hydrodesulfurization of 4,6-dimethyldibenzothiophene and dibenzothiophene over alumina-supported Pt, Pd, and Pt-Pd catalysts," *Journal of Catalysis*, vol. 242, no. 1, pp. 207–216, 2006.
- [16] C. T. Tye and K. J. Smith, "Hydrodesulfurization of dibenzothiophene over exfoliated MoS₂ catalyst," *Catalysis Today*, vol. 116, no. 4, pp. 461–468, 2006.
- [17] H. Nava, C. Ornelas, A. Aguilar, G. Berhault, S. Fuentes, and G. Alonso, "Cobalt-molybdenum sulfide catalysts prepared by in situ activation of bimetallic (Co-Mo) alkylthiomolybdates," *Catalysis Letters*, vol. 86, no. 4, pp. 257–261, 2003.
- [18] M. C. Kerby, T. F. Degnan, D. O. Marler, and J. S. Beck, "Advanced catalyst technology and applications for high quality fuels and lubricants," *Catalysis Today*, vol. 104, no. 1, pp. 55–63, 2005.
- [19] H. Farag and H. Al-Megren, "Textural characterizations and catalytic properties of quasispherical nanosized molybdenum disulfide," *Journal of Colloid and Interface Science*, vol. 332, no. 2, pp. 425–431, 2009.
- [20] International Centre for Diffraction Data, *JCPDS Powder Diffraction File*, International Centre for Diffraction Data, Swarthmore, PA, USA, 2000.
- [21] H. Farag, "Hydrodesulfurization of dibenzothiophene and 4,6-dimethyldibenzothiophene over NiMo and CoMo sulfide catalysts: kinetic modeling approach for estimating selectivity," *Journal of Colloid and Interface Science*, vol. 348, no. 1, pp. 219–226, 2010.
- [22] G. Delvaux, P. Grange, and B. Delmon, "X-ray photoelectron spectroscopic study of unsupported cobalt-molybdenum sulfide catalysts," *Journal of Catalysis*, vol. 56, no. 1, pp. 99–109, 1979.
- [23] P. Grange, "Catalytic hydrodesulfurization," *Catalysis Reviews*, vol. 21, no. 1, pp. 135–181, 1980.
- [24] M. Daage and R. R. Chianelli, "Structure-function relations in molybdenum sulfide catalysts: the "rim-edge" model," *Journal of Catalysis*, vol. 149, no. 49, pp. 414–427, 1994.
- [25] F. E. Massoth, G. Muralidhar, and J. Shabtai, "Catalytic functionalities of supported sulfides II. Effect of support on Mo dispersion," *Journal of Catalysis*, vol. 85, no. 1, pp. 53–62, 1984.
- [26] B. Scheffer, P. J. Mangnus, and J. A. Moulijn, "A temperature-programmed sulfiding study of NiO₃/Al₂O₃ catalysts," *Journal of Catalysis*, vol. 121, no. 1, pp. 18–30, 1990.
- [27] P. A. Nikulshin, D. I. Ishutenko, A. A. Mozhaev, K. I. Maslakov, and A. A. Pimerzin, "Effects of composition and morphology of active phase of CoMo/Al₂O₃ catalysts prepared using Co₂Mo₁₀-heteropolyacid and chelating agents on their catalytic properties in HDS and HYD reactions," *Journal of Catalysis*, vol. 312, pp. 152–169, 2014.
- [28] A. Pimerzin, A. Mozhaev, A. Varakin, K. Maslakov, and P. Nikulshin, "Comparison of citric acid and glycol effects on the state of active phase species and catalytic properties of CoPMo/Al₂O₃ hydrotreating catalysts," *Applied Catalysis B: Environmental*, vol. 205, pp. 93–103, 2017.
- [29] B. Vogelaar, N. Kagami, A. van Langeveld, S. Eijsbouts, and J. A. Moulijn, "Active sites and activity in HDS catalysis: the effect of H₂ and H₂S partial pressure," *American Chemical Society, Division of Fuel Chemistry*, vol. 48, no. 2, pp. 548–549, 2003.
- [30] N. Hermann, M. Brorson, and H. Topsøe, "Activities of unsupported second transition series metal sulfides for hydrodesulfurization of sterically hindered 4,6-dimethyldibenzothiophene and of unsubstituted dibenzothiophene," *Catalysis Letters*, vol. 65, no. 4, pp. 169–174, 2000.
- [31] T. Kabe, Y. Aoyama, D. Wang et al., "Effects of H₂S on hydrodesulfurization of dibenzothiophene and 4,6-dimethyldibenzothiophene on alumina-supported NiMo and NiW catalysts," *Applied Catalysis A: General*, vol. 209, no. 1–2, pp. 237–247, 2001.
- [32] H. M. Nakamura, K. Amemiya, and K. Ishida, "Inhibition effect of hydrogen sulfide and ammonia on NiMo/Al₂O₃, CoMo/Al₂O₃, NiCoMo/Al₂O₃ catalysts in hydrodesulfurization of dibenzothiophene and 4,6-dimethyldibenzothiophene," *Journal of the Japan Petroleum Institute*, vol. 48, no. 5, pp. 281–289, 2005.
- [33] V. S. Rabarahoela-Rakotovo, G. Brunet, F. Perot, and F. Diehl, "Effect of H₂S partial pressure on the HDS of dibenzothiophene and 4,6-dimethyldibenzothiophene over sulfided NiMoP/Al₂O₃ and CoMoP/Al₂O₃ catalysts," *Applied Catalysis A: General*, vol. 306, pp. 34–44, 2006.
- [34] E. Krebs, B. Silvi, and P. Raybaud, "Mixed sites and promoter segregation: a DFT study of the manifestation of Le Chatelier's principle for the Co(Ni)MoS active phase in reaction conditions," *Catalysis Today*, vol. 130, no. 1, pp. 160–169, 2008.
- [35] Y. Sun and R. Prins, "Mechanistic studies and kinetics of the hydrodesulfurization of dibenzothiophene on Co-MoS₂/γ-Al₂O₃," *Journal of Catalysis*, vol. 267, no. 2, pp. 193–201, 2009.
- [36] G. Nadege, C. Tivadar, R. Pascal, G. Christophe, and V. Michel, "Influence of H₂S on the hydrogenation activity of relevant transition metal sulfides," *Catalysis Today*, vol. 98, no. 1–2, pp. 61–66, 2004.
- [37] H. Farag, K. Sakanishi, M. Kouzu, A. Matsumura, Y. Sugimoto, and I. Salto, "Dual character of H₂S as promoter and inhibitor for hydrodesulfurization of dibenzothiophene," *Catalysis Communications*, vol. 4, no. 7, pp. 321–326, 2003.
- [38] N. Guernalec, C. Geantet, P. Raybaud, T. Cseri, M. Aouine, and M. Vrinat, "Dual effect of H₂S on volcano curves in hydrotreating sulfide catalysis," *Oil and Gas Science and Technology- Revue de l'IFP*, vol. 61, no. 4, pp. 515–525, 2006.
- [39] H. Toulhoat, P. Raybaud, S. Kasztelan, G. Kresse, and J. Hafner, "Transition metals to sulfur binding energies relationship to catalytic activities in HDS: back to sabatier with first principle calculations," *Catalysis Today*, vol. 50, no. 3–4, pp. 629–636, 1999.



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