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Research Note

Investigation of 4,6-dimethyldibenzothiophene hydrodesulfurization over a highly active bulk MoS_2 catalyst

Hamdy Farag * and Kinya Sakanishi

Institute for Energy Utilization, AIST, Tsukuba West, Ibaraki 305-8569, Japan

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Abstract

The hydrodesulfurization (HDS) of 4,6-dimethyldibenzothiophene was investigated in a batch-stirred microautoclave reactor over a laboratory-synthesized MoS_2 catalyst. The reaction was found to proceed through two main parallel pathways: direct desulfurization (DDS) and hydrogenation (HYD). The effect of a wide range of H_2S concentrations on the HDS activity and selectivity was studied. Contrary to the well-known inhibition of HDS caused by H_2S, the global catalytic activity of HDS was enhanced more than two times with inclusion of H_2S in the reaction zone. The increase in the activity is attributed to a significant enhancement in the hydrogenation reaction route, while the direct desulfurization products were only slightly affected. It is suggested that H_2S modifies the active sites so that they can be exploited more efficiently in the hydrogenation reaction.

Keywords: Hydrodesulfurization; MoS_2; H_2S; 4,6-Dimethyldibenzothiophene

1. Introduction

Hydrodesulfurization (HDS) is of considerable interest to the oil refining industry as the global environment becomes more concerned. The relative reactivity of sulfur-containing species varies significantly with the identity of the molecular structure and the substituent location to the sulfur atom. Polyaromatic thiophenes are considered to be the most refractory sulfur species. They constitute the major portion of sulfur in the high-boiling fraction of crude oil, i.e., heavy naphtha, diesel, and light FCC naphtha. The order of their reactivity has a strong relationship with the selectivity involved in the reaction [1–6]. In general, the HDS reaction of thiophene (the most reactive aromatic sulfur species) occurs much more readily via the direct desulfurization pathway, i.e., hydrogenolysis of the C–S bond. On the other hand, the HDS of 4,6-dimethyldibenzothiophene (4,6-DMDBT) (the main refractory target for deep HDS) operates with a significant contribution from the hydrogenation pathway. Nevertheless, the contribution percentage of each reaction route to the ultimate catalytic activity at fixed reaction conditions is entirely ruled by the catalyst identity.

On looking for a hydrogenation pathway as a prospective alternative choice to overcome the steric hindrance barrier of these alkylated dibenzothiophene species, it is desirable to obtain as effective a hydrogenation catalyst as possible [7–11]. In a previous study [12], it was observed that the HDS of DBT over a bulk MoS_2 catalyst occurred principally through incorporation of the hydrogenation pathway in which phenylcyclohexane was the predominant product. The preliminary results showed the possibility of obtaining highly active bulk MoS_2 hydrogenation catalysts. It is interesting and surprising that the activity of this MoS_2 catalyst for DBT HDS was enhanced remarkably by the presence of H_2S in the feed. Thus, it would be of interest to extrapolate, broaden, and demonstrate the HDS investigation over this catalyst to the more refractory sulfur compounds such as 4,6-DMDBT, and this is the main aim of the present study. The effect of H_2S on the catalytic properties of the synthesized MoS_2 is analyzed.

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* Corresponding author.
E-mail address: hamdy-farag@aist.go.jp (H. Farag).

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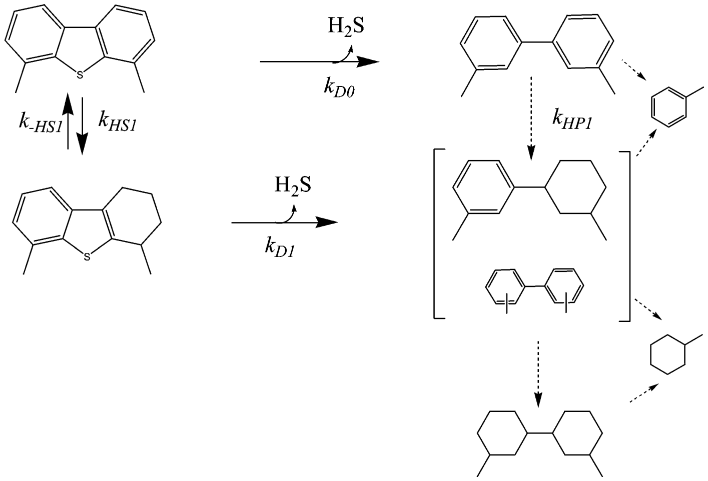


Fig. 1. Hydrodesulfurization reaction network of 4,6-DMDBT over MoS_2 catalyst at 340 °C and 3 MPa H_2.

2. Experimental

Details of the MoS_2 synthesis procedure have been presented elsewhere [13]. In brief, the ammonium heptamolybdate, AHM, precursor was annealed at 800 °C at a rate of 10 °C/min with a flowing gas mixture of (10% v/v) H_2S/H_2, 60 SCCM, from the beginning of the heating. Thereafter, the catalyst was ground for 24 h in air using a media-agitating mill that leads to a particle size of ca. 4 nm, as confirmed from the X-ray diffraction pattern, and a BET area of 118 m^2/g. A Mo (10 wt%)/γ-Al_2O_3 catalyst was prepared by conventional impregnation from AHM and sulfided at 400 °C by 10% v/v H_2S/H_2 prior to reaction. Catalytic tests were performed in a stirred batch 100-ml microautoclave reactor. The Feedstock of 0.1 wt% 4,6-DMDBT in decane was subjected to HDS investigation. All runs were carried out at 340 °C under 3 MPa H_2. The reaction was typically performed as follows: The reactor was charged with the catalyst powder (0.1 g) and 10 g of 0.1 wt% 4,6-DMDBT solution; 0.4 g copper powder was sometimes added to enable the reaction to be studied in an environment free of H_2S (the role of copper powder is to act as a scrubber for H_2S) [3]. The effect of various concentrations of H_2S on the HDS reaction of 4,6-DMDBT was studied. The external feeding of H_2S was accomplished by inserting a predetermined amount of sulfur powder into the feed. The measured amounts of H_2S by GASTEC gas detector (Model SG4010) at the end of the HDS runs refer to the almost fully transformation of sulfur to H_2S. The reaction products were analyzed using GC–FID (Agilent HP6890) and GC–MS (HP5970) equipped with a capillary methylsiloxane column (0.32 mm × 50 m).

3. Results

The main observed reaction products were 3,3′-dimethylphenylcyclohexane, 3,3′-dimethylbiphenyl, and partially hydrogenated tetrahydro-4,6-dimethyldibenzothiophene (H4-4,6-DMDBT). Traces of isomers of dimethylphenylcyclohexane, dimethylbiphenyl, dimethyldibenzothiophene, and 3,3′-dimethylbicyclohexane were detected. Interestingly, traces of dibenzothiophene were detected as well. Their corresponding desulfurized species were confirmed. The suggested reaction pathways for the HDS of 4,6-DMDBT are shown in Fig. 1. The individual reaction rate constants were obtained from a nonlinear numerical Runge–Kutta fitting of the experimental data on the assumption of first-order kinetics for each step in this reaction scheme [14].

The mechanism was classified into two reaction routes, hydrogenation that leads to the partially hydrogenated H4-4,6-DMDBT and its isomers, and direct desulfurization that leads to 3,3′-dimethylbiphenyl. The subsequent reaction products from these two routes are 3,3′-dimethylphenylcyclohexane and 3,3′-dimethylbicyclohexane. The partially hydrogenated H4-4,6-DMDBT (predominant) and the other derivatives containing the mother nucleus of dibenzothiophene were treated collectively as one species.

3.1. 4,6-DMDBT HDS in an environment free of H_2S

Fig. 2 shows the product distribution curves for the HDS reaction of 4,6-DMDBT over the MoS_2 catalyst in an environment almost free from H_2S (copper addition run; note that a considerable concentration of H_2S after this HDS run was measured indicating the limited efficiency of copper powder to trap H_2S). The isomerized and hydrocracked trace products in HDS of 4,6-DMDBT are a result of the acidic nature of this catalyst. The yield of the partially hydrogenated H4-4,6-DMDBT exhibits a maximum of about 54% from the overall conversion. The result implies that the partially hydrogenated H4-4,6-DMDBT species is an essential intermediate in the hydrogenation reaction route and is not being thermodynamically limited under the present reaction conditions.

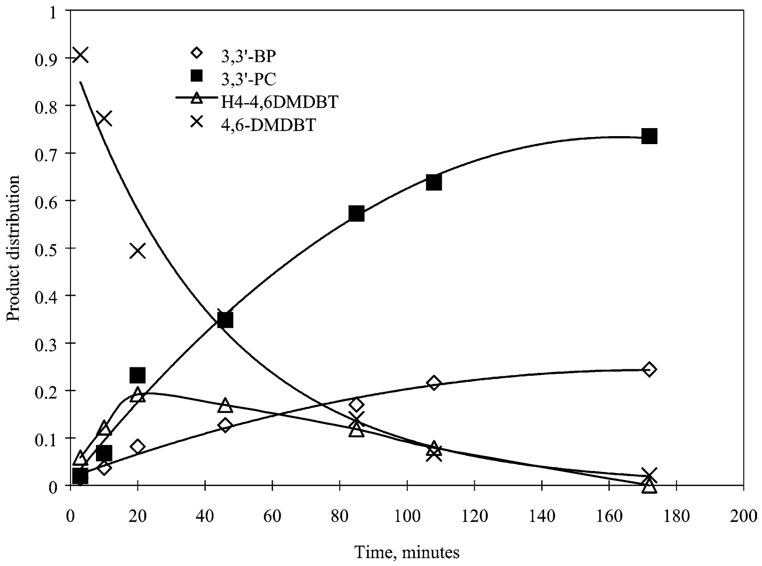


Fig. 2. Product distribution in the HDS of 4,6-DMDBT over MoS_2 catalyst in approximately free environment of H_2S at 340 °C and 3 MPa H_2.

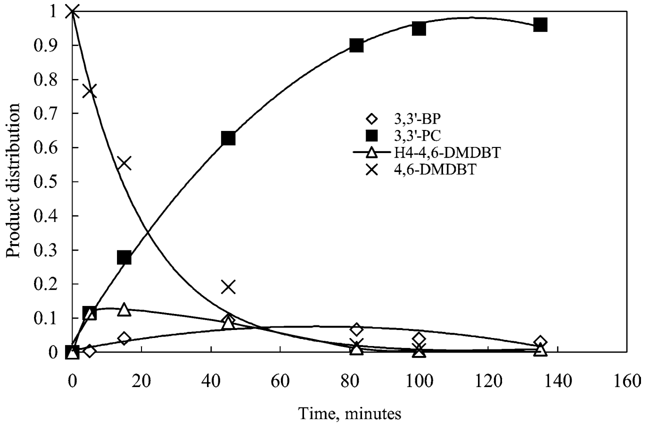


Fig. 3. Product distribution in the HDS of 4,6-DMDBT over MoS_2 catalyst in a mild(self) environment of H_2S at 340 °C and 3 MPa H_2.

3.2. 4,6-DMDBT HDS in an environment of H_2S

The influence of a wide range of H_2S concentrations was studied by adding sulfur powder to the feedstock. Fig. 3 shows that when self-produced H_2S remains in the reaction it remarkably enhances the HDS activity of 4,6-DMDBT. The enhancement in HDS activity has to be attributed to H_2S since the various reaction conditions for all runs were kept unaltered. The product distributions of 4,6-DMDBT HDS (run when self-produced H_2S from the reaction remained in the feed) showed almost entirely the involvement of the hydrogenation reaction route. The influence of various H_2S concentrations on the catalytic activity is shown in Fig. 4. The achievement of a high HDS catalytic activity for runs performed with inclusion of H_2S basically originates from the increase in activity in the hydrogenation route. Furthermore, one can note the steady catalytic activity in the presence of even a significant amount of H_2S. Fig. 5 shows a comparison between the catalytic activity of bulk MoS_2, Mo/γ-Al_2O_3, and a commercial CoMo/Al_2O_3 catalysts. The activity was normalized per gram weight of the active MoS_2 phase. Obviously, bulk MoS_2 exhibits the highest activity. Moreover, in terms of the catalyst volume (MoS_2, 4.8–5 g/cm^3; CoMo/Al_2O_3, 0.7–0.9 g/cm^3), the catalytic activity of this bulk MoS_2 is highly superior.

4. Discussion

The results described above report a unique interesting character of H_2S in not being an inhibitor but rather a promoter for the catalytic HDS reaction. However, before we analyze these data further it is important to clarify any suspicious assumptions of this performance. Thus, one may wonder about the possibility of this catalyst being partially oxidized, in which case the presence of H_2S would possibly bring it into a sulfide form, which is well known to be more active than the oxide form. Accordingly, the promotion could be due to the resulting sulfide phase and not essentially to the presence of H_2S itself. As this is a reasonable explanation for the present behavior, we investigated the reproducibility of the results. Another set of HDS experiments was carried out over the milled MoS_2 catalyst that was freshly sulfided by 10 v/v% H_2S/H_2 at 400 °C prior to reaction. We have further performed another in situ HDS experiment in which the MoS_2 was resulfided and loaded into the autoclave along with the reactant solution and iron powder using a glove box under Ar atmosphere. The results are included in Fig. 4. As can be seen, almost identical behavior was obtained, thus excluding the possibility of the activity enhancement being due exclusively to the sulfide form species, especially for runs operated at an H_2S level that is 10 of orders higher than the quantitative needs for full sulfidation of the catalyst. Moreover, the coincidence between the catalytic activity of 4,6-DMDBT HDS and H_2S is

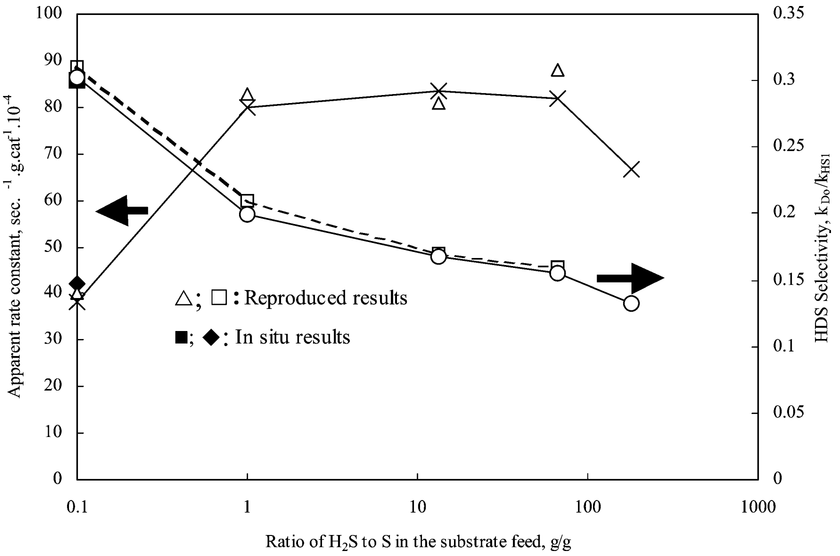
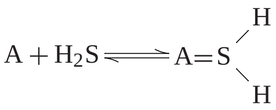


Fig. 4. Effect of inserted H_2S level on the ultimate HDS activity and selectivity of 4,6-DMDBT over MoS_2 catalyst at 340 °C and 3 MPa H_2. △, □: Reproduced activity and selectivity results obtained over the milled MoS_2 after fresh sulfidation, respectively. ◆, ■: In situ HDS activity and selectivity results, respectively.

demonstrated practically in a circular reversible manner, i.e., keeping H_2S in the reaction medium increases the activity while taking it out drastically reduces it. The present results then may indicate the involvement of H_2S in the HDS reaction mechanism through modifying the potentially catalytic active sites, as suggested below.



$$A + H_2S \rightleftharpoons A{=}S\begin{smallmatrix}H\\ \\ H\end{smallmatrix}$$

The enhancement in activity with H_2S was originally attributed to the tremendous promotion that occurred in the hydrogenation route, i.e., k_{HS1}, while the direct desulfurization, k_{D0}, was not greatly affected. Fig. 4 describes the influence of H_2S on the reaction selectivity, defined as the ratio of the apparent rate constant for DDS to the apparent rate constant for HYD, i.e., k_{D0}/k_{HS1}. As the H_2S concentration increases, the selectivity shifts smoothly toward a higher involvement of the hydrogenation route. These results support the view that two distinct catalytically active sites exist for each reaction pathway. H_2S is proposed to chemically interact with the catalyst producing new sites that are active for HYD.

Unlike the conventional observation of inhibition resulting from H_2S in the HDS for both real feed and refractory sulfur compounds, the present results showed a clear improvement in the catalytic activity in the presence of even a significant amount of H_2S. In a trickle bed reactor the oil stream flows so that the produced H_2S accumulates to reach its highest concentration at the reactor outlet. Consequently, the downstream part of the catalyst bed has to operate in a regime with a relatively high concentration of H_2S. Thus, a catalyst that behaves positively with H_2S is worthy of more morphological and structural investigations.

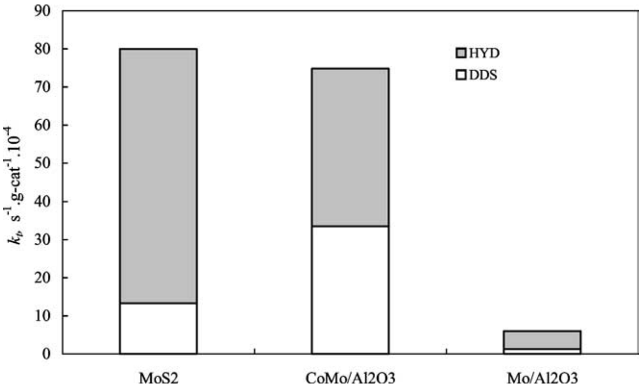


Fig. 5. Activity in the HDS of 4,6-DMDBT over MoS_2, $CoMo/Al_2O_3$ commercial, and $Mo/\gamma\text{-}Al_2O_3$ catalysts at 340 °C and 3 MPa H_2. The activity was normalized on the weight of MoS_2 phase.

Inhibition due to the effect of H_2S on the HDS activity of DBT and/or 4,6-DMDBT over a conventional alumina-supported Mo, CoMo, and/or NiMo catalyst has been observed and documented in the literature [15–18]. The influence of H_2S depends, however, on the HDS conversion and on the nature of the catalyst. The effect was found to be more pronounced for the direct desulfurization route than for the hydrogenation route. Industrially, catalysts for the HDS of real feedstocks inevitably operate in an environment containing H_2S. The impact of H_2S on the catalyst behavior will permanently remain; hence, it is one of the HDS by-products. The HDS selectivity depends on the nature of the polyaromatic sulfur species that are processed, the reaction conditions, and the catalyst. The first two factors cannot be widely changed because the real gas oil feed already contains the most refractory sulfur species and applying severe operating reaction conditions is limited. Thus, the only factor that eventually rules the selectivity in the deep hydrodesulfurization extent is the catalyst identity. Two options of interest have been described in the literature to overcome the refractory nature caused by the steric hindrance of the alkylated substituents close to the sulfur atom: one is to exploit isomerization, and the other is to focus on better hydrogenation catalysts [19–25]. The latter option is more interesting, as the isomerization catalysts can easily be deactivated during reaction. The activity promotion due to H_2S, observed in the present work, is a distinct pioneering phenomenon, specific only to this bulk catalyst.

5. Conclusion

A clear enhancement in the HDS of 4,6-DMDBT over MoS_2 was observed with incorporation of H_2S. The development of the activity is mainly attributed to the enhancing activity of the hydrogenation pathway, as 3,3′-dimethylphenylcyclohexane was the major reaction product. H_2S is suggested to be involved in the HDS reaction mechanism. The observation of the positive increase of MoS_2 activity with H_2S could open a new research area in which an additional variety of catalytic hydrotreating is feasible. Processes that take advantage of the high hydrogenation activity of this catalyst may be worthwhile to pursue.

Acknowledgment

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