DIBENZOTHIOPHENE HYDRODESULFURIZATION OVER BULK UNPROMOTED AND COBALT PROMOTED MoS_2 CATALYSTS

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Introduction

Environmental concerns are the driving force behind the growing interest of removing sulfur compounds from middle distillate fuels. To encounter the strict of nowadays regulation of sulfur content superior, catalyst is needed. Polyaromatic sulfur compounds are confirmed to be the real obstacle for deep hydrodesulfurization (HDS) reaction. They are the leftover species after deep HDS. These species react through consecutive and sequence reaction in which the selectivity plays a role in the reaction mechanism. In respect to this, catalyst designers encounter two options; one is to search for a catalyst in which the hydrogenation is the pioneer feature of its activity and the other is an ascertained catalyst for the hydrogenolysis of C-S bond. MoS_2 based catalysts are widely applied for HDS reactions. The role of cobalt in promoting MoS_2 supported catalysts has been extensively studied and the synergetic effect is well established.1,2 Nevertheless, the impact of cobalt addition to bulk MoS_2 on the selectivity trend of HDS is not clear yet. A better understanding how cobalt may modify the bulk MoS_2 catalyst will provide researchers with fruitful information about how such inclusions promote the HDS activity in case of supported Mo-catalysts. In this piece of work we address some experimental insight work on the comparison between behavior of bulk and supported Mo-catalysts. In addition, it may contribute the linkage between the catalytic activity and selectivity in HDS reaction. Kinetic treatments that focus on the selectivity change of HDS of dibenzothiophene (DBT) are prescribed.

Experimental

Bulk MoS_2 was synthesized through heat annealing in presence of continuous flow of 10v/v% H_2S/H_2 gas mixture. Detail of preparation and characterization of this catalyst is stated elsewhere3. The obtained highly crystalline MoS_2 phase was further ground fine particle around nanometer sizes. This form of MoS_2 was applied to be a primary support for cobalt addition. Alcoholic solution of cobalt (II) acetate was impregnated to MoS_2 at ambient temperature. This mixture was exposed to ultrasonic for 10min. Then the sample was dried at 80°C under vacuum condition. Thereafter, the catalyst was pre-sulfided at 400°C by flow of 10v/v H_2S/H_2 gas mixture. CoS phase synthesized via heat annealing of cobalt (II) acetate with gas flow of 10v/v%H_2S/H_2.

The HDS catalytic activity of DBT was investigated through the use of a batch magnetically stirrer micro-autoclave reactor. All reaction runs were examined at 340°C and 3MPa H_2. Some reaction runs were carried out after addition of copper powder which serves as a scrubber of the continuous production of H_2S during HDS. Reaction products were tracked by the aid of GC-FID and GC-MS.

Results and Discussion

The main HDS products from DBT obtained over the studied catalysts are biphenyl (BP) and Phenylcyclohexane (PC) in addition to the well-known intermediate of H4-DBT. However, it is unique of the MoS_2 and/or Co-promoted bulk MoS_2 catalysts that traces of fragmented products like alkylated derivatives of benzene or even naphthalene is formed. The presence of these species could be explained due to a series of consecutive hydrogenation reactions that takes place over this kind of catalysts. Table 1 shows the catalysts characterization and the product distribution of DBT HDS at ca. 50% conversion level. Fixed conversion level was adopted because the selectivity of these consecutive and parallel reactions varies with the conversion level.

Table 1. Activity of Bulk MoS_2 Promoted Cobalt Catalysts for DBT HDS.

Catalyst	Co wt%	Level of H_2S^a	HDS*	Selectivity at 50% conv. level		
				BP	PC	H4-DBT
CoS	100	High	2	24.4	21.6	3.9
MoS_2	0	Low	24	22.3	25.3	2.4
MoS_2	0	High	83	8.2	28.5	13.3
MCS-I	2	High	38	28.5	16.4	5.1
MCS-II	10	High	33	28.5	16.3	5
MCS-III	16	Low	17	43.2	6.2	0.7
MCS-III	16	High	33	28.6	16.7	5.2

*$s^{-1}.g.cat.^{-1}.10^{-4}$, (340°C & 3MPa H_2), ± 3%

The HDS activity of CoS is very low compared with MoS_2 catalyst. One may notice the sharp decrease in activity for Co-promoted MoS_2 catalysts. Unlike the supported CoMo catalysts, Co addition to bulk MoS_2 has a negative effect on the HDS activity. In addition the selectivity of DBT HDS was changed dramatically based on the level of H_2S in the reaction medium. **Figures** 1,2 and 3 show the activity and selectivity behavior of the MoS_2 and Co-promoted MoS_2 catalysts. To explain the connection between cobalt inclusions and the changes in HDS activity, one must look at their impact on the selectivity trend.

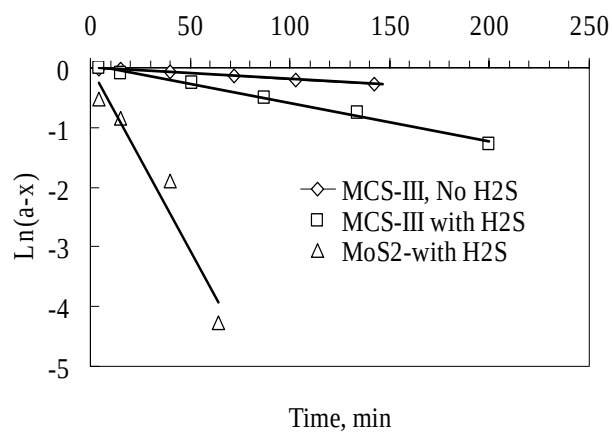

Figure 1. Pseudo-first order plots of DBT HDS over MoS_2 and MCS-III catalysts with or without copper addition.

It is interesting to note the drastic change in selectivity in presence or absence of Co. The obvious decrease of activity with Co inclusions to MoS_2 is markedly linked in a direct proportion relation with the change made on the selectivity behavior. This raises the consolidation between selectivity and activity in HDS reaction4. Another interesting feature of the present results is the effect of H_2S on the selectivity and activity of DBT HDS. Figures 3 and 4 show the effect of H_2S level on the HDS selectivity of DBT over MCS-III catalyst. H_2S level is defined as whether copper are included or not into the reaction medium. It is evident that H_2S promote the reaction via the acceleraton of the hydrogenation route. Nevertheless, the contribution from the direct hydrogenolysis route is still significant. DBT HDS showed pseudo-first order behavior and the influence of H_2S on the activity is clarified on **Figure** 1. **Figures** 2 and 3 illustrate the selectivity changes over MoS_2 and MSC-III catalyst. The hydrocracked fragments products were assumed to result from PC.

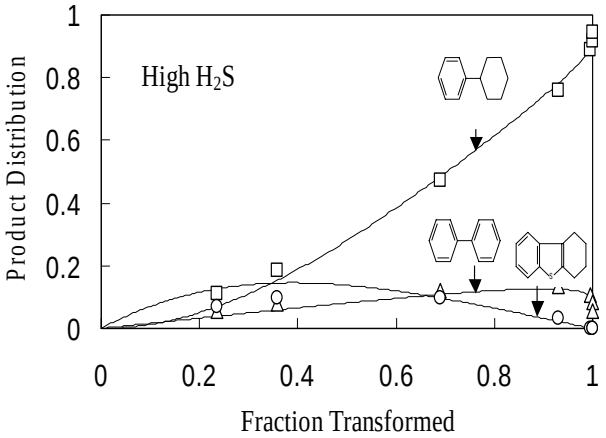

Figure 2. HDS selectivity Curves of DBT (MoS_2, 340 °C & 3MPa H_2).

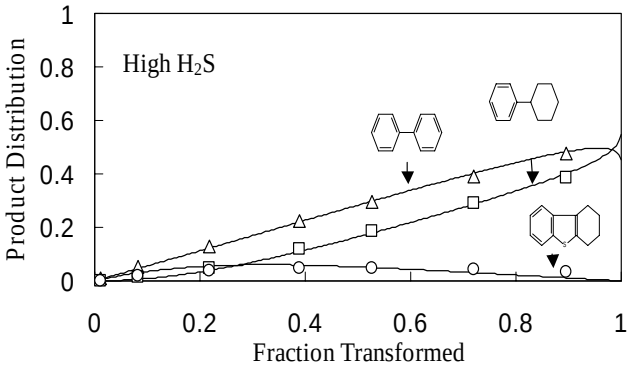

Figure 3. HDS selectivity Curves of DBT (MCS-III, 340 °C & 3MPa H_2).

The decrease in activity of MoS_2 after inclusion of Co is suggested to be due to the negative synergetic effect that has been widely known for these supported catalysts. In other words, the synergy in the present bulk sulfides is not helpful for HDS activity. It seems that this synergy rule the HDS reaction via more contribution of the direct desulfurization route leading to BP species. The reaction through this route is reported to undergo geometrical difficulty to reach the prospected catalytic active sites. In this respect, it is suggested that the catalytic activity is linked with two distinct active sites. The inclusions of Co to the MoS_2 catalyst replaced some of the usable hydrogenation sites in MoS_2 catalyst. Consequently, these sites will no longer be active for hydrogenation. The obtained new sites forward the reaction to the direct desulfurization route.

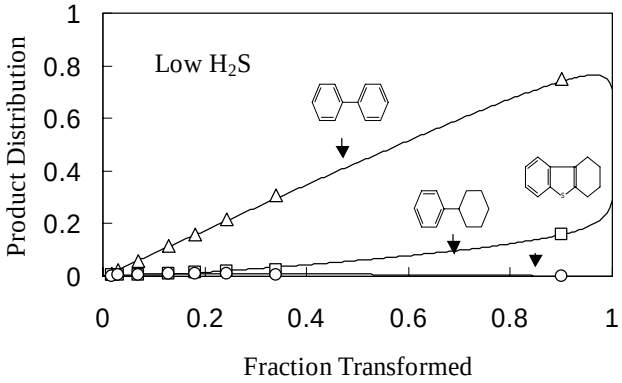

Figure 4. HDS product distribution curves of DBT over MCS-III catalyst, the run with added copper powder. (340°C & 3MPa H_2)

In summary, the results show the close correlation between activity and selectivity in HDS reaction and how cobalt modified the HDS reaction mechanism occurred over MoS_2 catalyst.

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