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The effect of additives on hydrodesulfurization of dibenzothiophene over bulk molybdenum sulfide: Increased catalytic activity in the presence of phenol

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ABSTRACT

The effect of various additive organic reagents on the activation of MoS₃ as molybdenum sulfide catalyst precursor during hydrodesulfurization reaction of dibenzothiophene was studied. It was found that the presence of phenol or 1-naphthol greatly promoted the activity of the catalyst, while tetralin, 9,10-dihydrophenanthrene, ethylbenzene, and pyridine reagents were found to be detrimental for the activity of the catalyst.

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1. Introduction

The heterocyclic thiophenic compounds are the most frequently encountered sulfur containing products in coal derived liquids and in petroleum [1–3]. They are detrimental to the stability of the fuels and are also forced to limit their presence due to environmental constraints. Among sulfur containing organic species, dibenzothiophene derivatives are commonly considered to be the most resistant to the hydrodesulfurization (HDS). Their high stability and thus, high resistance against desulfurization challenged many researchers to develop catalysts and improve techniques for effective desulfurization of these compounds and to understand the mechanism of relevant processes. The methods proposed to eliminate them, as reviewed by Song and Ma involve HDS, oxidation, and biodesulfurization [3]. Nevertheless today's industrial method relies on the HDS process in which alumina supported Mo/Co or Mo/Ni metal combinations are the main catalyst types that are used.

Although the relevant literature is huge and contributes much in understanding of these catalytic reactions, there are still much to do especially in mixed systems because in HDS of either petroleum or coal-derived liquids there are always

various classes of compounds that may interfere with the desulfurization reactions. There are a number of studies that aimed at examination of the effect of such species on the catalytic activity in HDS; those additive types studied were aromatics [4–7], hydroaromatics [8], nitrogen containing basic aromatic reagents [4,9–14], and H₂S gas [15–19]. The presence of all was determined to be detrimental for HDS processes when performed over supported catalysts. Nevertheless only was the latter reagent, H₂S, tested for bulk Molybdenum sulfide catalyst and found, in contrast to those with supported ones, to be beneficial for the activity of the catalyst [18,19].

The majority of coal reserves of Turkey consist of low rank coals and most rich of organic sulfur content [20]. The direct combustion of those are unsuitable due to environmental constraints and wait for further processes through which sulfur free clean fuel products or chemical stocks would be produced. Molybdenum sulfide, known as the active molybdenum compound in catalysis of HDS process, has also high activity in direct coal liquefaction processes. There are a number of studies that utilized ammonium tetrathiomolybdate (ATTM) as a precursor compound to active molybdenum sulfide catalyst in liquefaction reactions [21–27]. The preference in use of this molybdenum compound, rather than direct use of

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MoS₂, is due to its appreciable solubility in water that allows one to be able to better disperse it over coal by impregnation.

In a recent study, ammonium heptamolybdate (AHM) was also used as a catalyst precursor for the liquefaction of high sulfur Turkish low rank coals [28]. Inherent sulfur content of the coals was assumed to be the source of the sulfur necessary in converting the AHM to an active molybdenum sulfide structure. The results indicated that the presence of the molybdenum compound produced oil fraction with less sulfur content, this being related with the desulfurization activity of the catalyst.

As oil fractions from low rank coals composed of mainly aliphatics, alkyl substituted aromatics, hydroaromatics and phenolic compounds [28], we decided to investigate the effect of these classes of compounds on the catalytic activity in HDS reaction. The molybdenum compound used within this study was MoS₃, which is known as stable intermediate in conversion of ATTM to active MoS₂ [24,25,29]. Of the additive reagents used in this study, tetralin and 9,10-dihydrophenanthrene (DHP) were hydrogen donor reagents often used at coal liquefaction studies and may also form by partial hydrogenation of coal liquefaction solvents and/or primary oil liquefaction products; pyridine represents nitrogenous species; and ethylbenzene and phenol, represent monoaromatic and phenolic structures, respectively.

2. Materials and methods

The chemicals and solvents used were obtained commercially and their purities were checked by GC-MS. AHM was transformed to ATTM by bubbling its aqueous ammonia solution with H₂S and then MoS₃ is obtained by acidification of ATTM [29]. In a typical hydrogenation experiment 3 g of hexadecane (13.2 mmol), 120 mg of dibenzothiophene (0.651 mmol), 120 mg of an organic additive and 50 mg of MoS₃ (0.26 mmol) were charged into a mini tubing-bomb reactor of 25 mL volume. After sealing the reactor, air inside the reactor was swept out by successive pressurizing (6.9 MPa cold) and depressurizing twice with nitrogen and twice with hydrogen gases. Finally the reactor was pressurized with hydrogen gas (6.9 MPa cold) and submerged into an eutectic salt bath after fixing on a horizontally oscillating system. The bath having a temperature of 5 °C above the desired working temperature, heats up the reactor to the desired working temperature in 1–2 min. The horizontally oscillating system shakes the reactor with amplitude of 2 cm at 400 cycles/min. The contents of the reactor were washed with acetone, filtered to separate the catalyst with the aid of an appropriate organic solvent and naphthalene or bibenzyl was added to the solution as an internal standard.

Reaction products were identified by gas chromatography-mass spectrometry (GC-MS) using a Hewlett-Packard Model 5890 II GC coupled with a Hewlett-Packard Model 5970 mass selective detector operating in the electron-impact mode at 70 eV. The column used was TC-17, 30 m long and 0.32 mm ID, coated with 50% phenyl-50% methyl polysiloxane with a coating film thickness of 0.5 μm. For quantification, an ATI Unicam 610 Series GC with a flame ionization detector and the same type of TC-17 column were used. Both GC and GC-MS were temperature programmed from 40 (5 min.) to 270 °C

(5 min.) at a rate of 6 °C/min. The results were given on the basis of mole percent of dibenzothiophene.

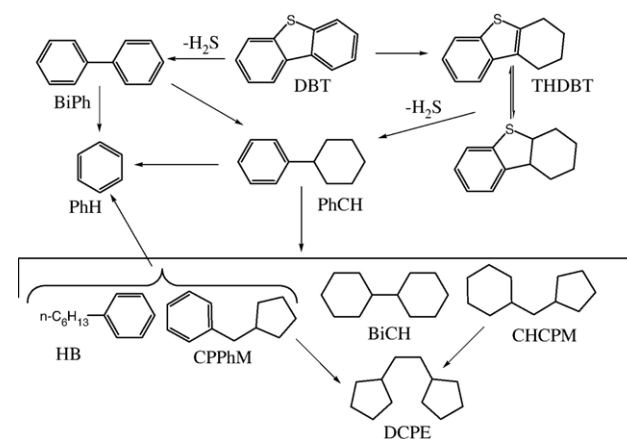
3. Results and discussion

3.1. Effect of phenolic compounds

The product slate of molybdenum sulfide catalyzed HDS reaction of DBT and possible reaction pathways are illustrated in Scheme 1. In agreement with previous reports HDS reaction seemed to proceed through two pathways; direct desulfurization and desulfurization subsequent to hydrogenation of one of the six membered ring [3]. The formation of isomeric and cracking products indicated that the catalyst had acidic nature as well.

Table 1 compares the effect of the presence of phenolic reagents over HDS activity of molybdenum sulfide. The molar mass balance was calculated to be better than 90% in all cases. The addition of phenol into the reaction medium in the presence of catalyst precursor had a dramatic effect on conversion and product slate at both 350 and 400 °C reaction temperatures. The addition of phenol increased HDS% from 15 to 47 and from 54 to 97 at the reaction temperatures of 350 and 400 °C, respectively. A comparable result was also obtained in the presence of 1-naphthol.

Not only did the catalyst activity enhance for HDS reaction, but its hydrogenation and hydrocracking activities were also promoted with the presence of phenol. Hydrogen introduction to aromatic moieties calculated, on a basis of H atoms/DBT converted, by taking into account the hydrogenated DBT product; 1,2,3,4-tetrahydrodibenzothiophene (THDBT) and the desulfurized hydrogenated products; phenylcyclohexane (PhCH), cyclopentylphenylmethane (CPPhM), hexylbenzene (HB), bicyclohexane (BiCH), cyclohexylcyclopentylmethane (CHCPM), and 1,2-dicyclopentylethane (DCPE), were 4.15 and 3.83 at 350 °C, and 6.22 and 4.97 at 400 °C, with and without added phenol, respectively. In addition, the increase in the molar amount of isomerization products (CPPhM, HB, BiCH, CHCPM, and DCPE) per HDS product from 0.228 to 0.336 at 400 °C evidenced the increased activity of the catalyst for



Scheme 1 – Possible reaction pathways for the hydrodesulfurization (HDS) of dibenzothiophene (DBT).

Table 1 – The effect of phenolic reagents on the HDS activity of the molybdenum sulfide catalyst

T, °C	Additive	Conversion %	HDS % ^a	Yield%								
				THDBT	BiPh	PhCH	CPPhM	HB	BiCH	CHCPM	DCPE	PhH
350	–	26	15	10	5	5	<1	<1	<1	<1	<1	2
350	Phenol	51	47	16	6	9	1	<1	3	3	1	31
400	–	66	54	12	15	16	4	1	5	5	2	5
400	Phenol	98	97	<1	26	29	11	1.4	9	14	6	95
400	4-NO ₂ C ₆ H ₄ OH	65	55	10	13	18	2	<1	8	3	2	9
400	2,6-di- <i>tert</i> -butylphenol	75	63	11	10	12	3	<1	4	4	2	27
400	1-naphthol	99	99	<1	19	26	9	1	9	13	5	19
400	H ₂ O	70	61	9	16	22	4	<1	6	4	1	8

^a HDS%: Conversion%-THDBT%.

hydrocracking reactions. However, the isomerization activity of the catalyst was not so dissimilar at the lower reaction temperature, 350 °C (0.1 without phenol vs. 0.12 with phenol). The controlled experiments showed that phenol had no direct involvement in HDS of DBT in the absence of catalyst.

Fig. 1 illustrates conversion kinetics of DBT. Sigmoidal kinetic plots were common pattern for the both reactions performed in the absence or presence of phenol at 400 °C, indicating that the catalysts passed through different phases in the course of reactions. The conversion rate of DBT was greatly lowered after about 15 minute of the reactions for the both reaction systems. The following HDS occurred mainly from THDBT in relatively slow rate in the absence of phenol

(Fig. 1a), however, with the presence of phenol, the catalyst regained its HDS activity after about 5 minute of an induction period and led to a 98% conversion after 30 min of the reaction (Fig. 1b), evidencing that the presence of phenol in situ regenerated the active sites of the molybdenum sulfide catalyst.

HDS reaction was also performed in the presence of two substituted phenol derivatives, 4-nitrophenol and 2,6-di-*tert*-butylphenol. The effect of the former reagent was negligible on the conversion of DBT at 400 °C. The presence of sterically congested the latter molecule moderately increased HDS from 54 to 63% at 400 °C. The promotive effect of phenol may be related to the deoxygenation process. In the absence of DBT, phenol itself was determined to undergo dehydroxylation to the extent of 81% under the respective conditions applied for HDS reaction at 400 °C, nevertheless the phenol conversion was about 50–55% in the presence of DBT after the 30 min of HDS reaction, probably due to competitive adsorption-reaction cycle. The dehydroxylation of those substituted phenols was much lower. These results may imply that the catalyst regeneration might be related with the dehydroxylation process of phenol. The dehydroxylation reaction yields water and one may consider that water might be the primarily responsible reagent in promoting the catalyst activity, nevertheless the effect of water was determined to be little on HDS reaction (Table 1).

To realize whether the presence of phenol in reaction medium is necessary or just the pretreatment of the catalyst precursor with phenol was enough before subjecting to the reaction, the catalyst precursor was treated under H₂ pressure with or without added phenol in the presence of hexadecane solvent, but in the absence of DBT at the reaction temperature of 350 or 400 °C and subsequently tested for their activities for HDS reaction in the absence of phenol. It can clearly be seen that the pretreatment greatly increased the activity of the catalyst regardless phenol is present in reaction medium or not (Table 2). The catalyst pretreated in the presence of phenol at 350 °C showed somewhat better activity than that treated in the absence of additive at the HDS reaction temperature of 350 °C. However, both the pretreated catalysts showed greatly higher HDS activities than did the untreated MoS₃.

The DBT conversion was almost complete with both catalysts pretreated at 400 °C with or without added phenol. However, from the yields of benzene and biphenyl products it seems that the pretreatment in the absence of phenol rendered the catalyst to have higher hydrocracking activity.

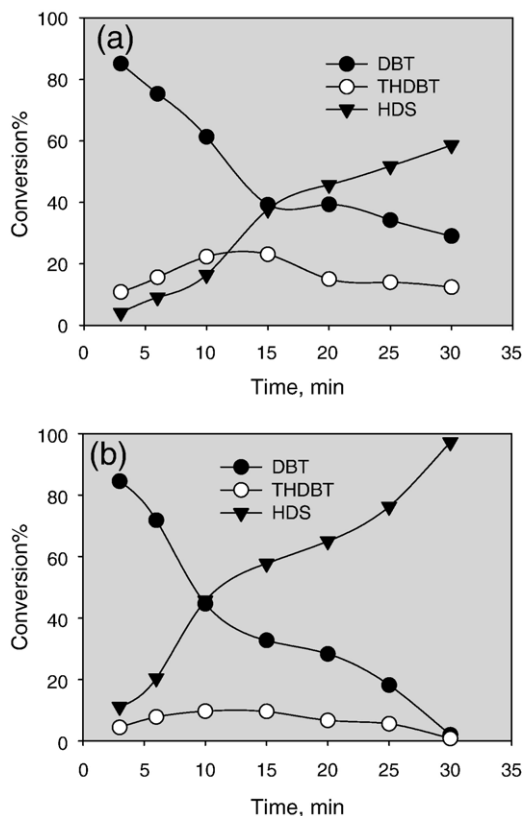


Fig. 1 – The conversion and HDS kinetics of DBT in the absence (a), and presence of phenol (b) at 400 °C.

Table 2 – The effect of phenol pretreatment on the HDS activity of the molybdenum sulfide catalyst^a

Pretreatment		Yield%										
T, °C ^b	Additive	Conversion%	HDS% ^c	THDBT	BiPh	PhCH	CPPhM	HB	BiCH	CHCPM	DCPE	PhH
350	No	86	76	10	13	31	5	<1	8	12	3	2
350	Yes	93	88	5	14	36	5	<1	9	13	4	6
400	No	>99	>99	<1	7	22	9	1	8	8	2	42
400	Yes	100	100	0	11	24	12	1	10	14	6	22

^a All reactions were carried out in the absence of any added organic additive.

^b Represents both pretreatment and reaction temperatures.

^c HDS%: Conversion%-THDBT%.

On the basis of these results it would not be so inappropriate to consider that the presence of phenolic reagents are useful for activating the molybdenum sulfide catalyst in HDS, hydrogenation and isomerization reactions when a catalyst precursor, such as ATTM or MoS₃ was used. However, the use molybdenum sulfide activated via pretreatment would be more active towards HDS reaction. Probably converting MoS₃ to active MoS₂ form, prior to HDS reaction, via heat treatment under H₂ pressure eliminated any factor that caused deactivation of the catalyst. MoS₃–MoS₂ transition liberates H₂S to the reaction medium. Our tests indicated that H₂S reagent formed is not responsible for the deactivation of the catalyst.

The factors that caused deactivation or activation of the catalyst are not clear at present. Nevertheless, BET surface analyses of the pretreated and used catalysts revealed that BET surface areas were in proximity for the samples pretreated at 400 °C with or without added phenol and the used catalyst recovered after the HDS reaction performed in the absence of phenol at 400 °C, varying between 32.9 to 34.4 m²/g, whereas that used catalyst recovered from the reaction performed in the presence of phenol at the reaction temperature of 400 °C had a BET surface area of 400 m²/g. We do not think that increased surface area is the only factor for the higher activity of the catalyst, because the pretreated catalysts as having lower surface areas would show lower activity otherwise. The detailed characterization of catalysts is under progress and will be presented elsewhere.

3.2. Effect of other compounds

The presence of non-phenolic other organic additives, used in this study, more or less reduced the HDS activity of the catalyst (Table 3). Including phenolic reagents the order of HDS activity of the catalyst varied as follow:

Phenol ≈ 1-naphthol > 2,6-di-tert-butylphenol > 4-NO₂C₆H₄OH > no additive > decalin > tetralin > ethylbenzene > DHP > pyridine.

Ishihara and Kabe [8] studied the solvent effects on the reaction of DBT over a commercial sulfided Co–Mo–Al₂O₃ catalyst. They found that the catalytic activity decreased in the following order: xylene > decalin > tetralin > n-hexadecane. This activity order was irreversibly related with the boiling points of the solvent.

Previously we tested the MoS₃ catalyst precursor for its activity in etheric aryl C–O cleavage under H₂ pressure. It was observed that hydrogen donor reagents remarkably reduced the C_{Ar}–O hydro-cleavage activity of the catalyst and this was related to the active hydrogen scavenging effect of the solvent that reduced active hydrogen concentration over the catalyst [30]. Such effect along with competitive adsorption of reagents may be responsible for the reduced activity of the catalyst toward HDS reaction. In keeping with the effect of hydrogen donor solvents on HDS determined, It was also found at the coal liquefaction studies of high sulfur low rank coals that the presence of tetralin caused production of oil fraction with higher sulfur contents compared to the tetralin free medium [28].

Finally, pyridine had the most deleterious effect on the HDS and hydrogenation of DBT. Pyridine, as a Lewis base probably deactivated the catalyst by electron donation to the active sites.

4. Conclusion

In this study, the HDS of DBT was studied with various organic additives at two different temperatures, 350 and 400 °C. The effect of each additive on the HDS of DBT has been studied and monitored separately. Hydrodesulfurization of

Table 3 – The effect of various organic additives on the HDS activity of the molybdenum sulfide catalyst

Additive	Conversion %	HDS % ^a	Yield%									
			THDBT	BiPh	PhCH	CPPhM	HB	BiCH	CHCPM	DCPE	PhH	
Decalin	62	51	11	15	18	3	<1	5	3	1	5	
Tetralin	59	46	13	15	13	3	<1	4	3	2	6	
DHP	50	37	13	12	9	2	<1	1	2	<1	9	
Ethylbenzene	56	41	14	10	11	3	<1	2	4	2	10	
Pyridine	35	21	13	9	7	<1	<1	4	1	<1	0	

^a HDS%: Conversion%-THDBT%.

thiophenic compounds present in petroleum or coal derived liquids by the catalysis of molybdenum compounds is affected in a different way by the other compounds present in the same liquid. Decalin does not have any effect, while a monoalkyl substituted benzene, hydroaromatics, and pyridine retarded the hydrodesulfurization of benzothiophene compounds. On the other hand phenolic and naphtholic structures that do not contain strong electron-withdrawing groups or bulky groups around the –OH group, promoted the HDS activity of BDT.

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