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Novel Bimetallic Dispersed Catalysts for Temperature-Programmed Coal Liquefaction

Technical Progress Report
October - December 1995

(Approved)

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Fuel Science Program
Department of Materials Science and Engineering
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ABSTRACT

Coal liquefaction involves cleavage of methylene, dimethylene and ether bridges connecting polycyclic aromatic units and the reactions of various oxygen functional groups. Here in this quarterly, we report on the catalytic effects of several molybdenum-, cobalt-, and iron-containing compounds in the reactions of dibenzothiophene (DBT) with hydrogen under conditions related to coal liquefaction.

The catalytic effects of several molybdenum-, cobalt-, and iron-containing compounds have been examined in the hydrogenation and hydrodesulfurization reactions of dibenzothiophene (DBT) under conditions related to coal liquefaction. The metal compounds are candidate catalyst precursors for direct coal liquefaction. The reactions were carried out in batch microautoclave reactors at 400°C for 30 minutes with 6.9 MPa (cold) hydrogen pressure, and tridecane solvent. A metal loading of 0.5 mol% resulted in low conversion and only hydrogenation. Addition of sulfur in 4:1 molar ratio led only to a minor increase in conversion and hydrodesulfurization. The use of a higher boiling solvent (octadecane vs. tridecane) was beneficial in providing increased conversion, hydrodesulfurization, and hydrogenation. An increase in metal compound loading to 36.2 mol% led to a dramatic increase in conversion, hydrodesulfurization, and hydrocracking. Molybdenum hexacarbonyl at 36 mol% loading, with added sulfur at 6:1 ratio and octadecane solvent, gave 100% conversion of dibenzothiophene to other products with 100% hydrodesulfurization. Ammonium tetrathiomolybdate and molybdenum(III) chloride are less active under similar conditions. A cobalt-molybdenum thiocubane complex gave unexpectedly low conversions. Iron and cobalt carbonyls also provided very low conversions, even with added sulfur.

Technical Progress

Reactions of Dibenzothiophene with Hydrogen in the Presence of Selected Molybdenum, Iron, and Cobalt Compounds as Catalyst Precursors

Introduction

Dispersing a catalyst onto the surface of coal particles provides good coal-catalyst contacting and facilitates hydrogenation during the early stages of liquefaction. Transition metal sulfides are attractive candidate liquefaction catalysts, because of their good hydrogenating abilities and resistance to poisoning. Molybdenum(IV) sulfide, MoS_2, is an example. The sulfides of interest are insoluble in common solvents, making it impossible to disperse them directly onto the coal from solution. Mixing a slurry of catalyst particles with coal particles may not give a good dispersion.[1] The use of so-called soluble catalyst precursors offers an alternative strategy. Catalyst precursors are soluble or insoluble compounds, that may themselves have little or no catalytic activity, but that decompose to form an active catalyst by the time the desired reaction temperature has been reached. A catalyst precursor used in a number of laboratories is ammonium tetrathiomolybdate, $(NH_4)_2MoS_4$, which undergoes thermal decomposition reactions leading eventually to MoS_2.[2]

Sulfided molybdenum catalysts have been used for years as hydrotreating catalysts in the petroleum industry. The addition of a first-row transition element, most commonly cobalt or nickel, "promotes" the activity of the catalysts. Sulfided cobalt-molybdenum catalysts, often on γ-alumina supports, are among the most commonly used hydrotreating catalysts.[3] The usefulness of cobalt sulfide / molybdenum sulfide catalysts for thiophene hydrogenation has been known for over sixty years.[4] The nature of the active species and the mechanism of catalytic action remains a subject of debate. For example, Delmon cataloged a dozen theories explaining behavior of these catalysts.[5] Topsøe and his colleagues established that the basic structural units are small MoS_2-like domains with Co atoms on the edges of the layers in the structure.[6,7] These investigators subsequently showed that these Co atoms on the edges of the MoS_2 layers seem to be located in the same plane as the Mo atoms, with a Mo-Co distance of 0.28 nm, which is close to that observed in Co-Mo-S cluster compounds.[8]

The heterocyclic thiophene structure is commonly considered the most resistant to hydrodesulfurization among the various kinds of organic sulfur functional groups likely to be found in coal liquids and petroleum. Among the family of thiophenes, resistance to desulfurization increases with molecular weight, which, in most cases, derives from increased

ring condensation, as, e.g., in the series thiophene < benzothiophene < dibenzothiophene. From these considerations, dibenzothiophene makes a convenient substrate for evaluation of hydrodesulfurization activity. This compound potentially can undergo several kinds of reactions in addition to hydrodesulfurization: hydrogenation to hydrodibenzothiophenes and hydrogenated products such as cyclohexylbenzene or bicyclohexyl; and hydrocracking to benzene or cyclohexane. Thus analysis of reaction products also provides insights into catalyst selectivity.

The present work aimed at understanding how the dispersed catalysts perform with respect to the reactions of polycyclic sulfur compounds under coal liquefaction conditions, since the reactions of sulfur-containing structures in coal and coal-derived liquids are inevitable during coal liquefaction using dispersed catalysts. It is not the purpose of this work to explore new dispersed catalysts or new processes for hydrodesulfurization (which is normally conducted using conventional supported catalysts). Our interest in studying the hydrogenation chemistry of dibenzothiophene derives from two concerns: first, an interest in using dibenzothiophene as a model compound to investigate activities and selectivities of a variety of monometallic compounds—mainly compounds of molybdenum—of potential use as catalyst precursors for coal liquefaction; and, second, to examine a bimetallic cobalt-molybdenum-sulfur compound as a catalyst precursor. In the present work we have not dispersed precursors onto coal particles; however, to be consistent with usage in a previous paper,[9] we retain the term "dispersed catalyst" to distinguish from conventional supported catalysts.

Experimental Section

Materials. Dibenzothiophene (98% purity), the various solvents (99% purity) and the monometallic catalyst precursors were obtained from commercial sources. The thiocubane-type complex $Cp_2Co_2Mo_2(CO)_2S_4$ (here Cp is cyclopentadienyl, C_5H_5) was synthesized according to the method of Brunner and Wachter.[10]

Reaction Procedures. Reactions of dibenzothiophene were carried out in horizontal microautoclave reactors (tubing bombs) of 33 mL capacity at 400°C for 30 min. The catalyst precursors were added at loadings of 0.5–36.2 mol% (of metal, not of the precursor compound itself) based on the mass of dibenzothiophene. Reactions with 0.5-5 mol% metal loading used about 8 mmol dibenzothiophene and 1.5 g solvent, and the runs with 36.2 mol% metal loading used 0.22 mmol dibenzothiophene and 4 g solvent. When sulfur was added, S/metal atomic ratios of 4 and 6 were used. The reactor was purged three times with hydrogen and then pressurized to 6.9 MPa at ambient temperature for all experiments. A preheated fluidized sand bath was used as the heat source. The reactor was vertically agitated at 240 strokes/min to provide mixing. After reaction, the hot reactor was quenched in cold water. The liquid contents were washed out with

dichloromethane through low-speed filter paper for qualitative and quantitative analysis of the filtrate. It should be noted that elemental sulfur was used in the experiments with sulfur addition. Sulfur combines readily with hydrogen to forms H_2S. Sulfur also combines with molybdenum, cobalt, iron, and many other metals easily. Our own research experience shows that the sulfidation of catalysts is more effective under H_2 pressure.

Analysis. Reaction products were identified by gas chromatography / mass spectrometry (GC/MS) using a Hewlett-Packard model 5890II GC coupled with a Hewlett-Packard model 5971A mass-selective detector operating in the electron-impact mode at 70 eV. The column used for GC/MS was a J & W type DB-17 column, 30 m long and 0.25 mm diameter, coated with 50% phenyl – 50% methyl polysiloxane with a coating film thickness of 0.25 µm. For quantification, a Hewlett-Packard model 5890II GC with a flame ionization detector and the same type of DB-17 column was used. Both GC and GC/MS were temperature programmed from 40 to 260°C at a rate of 4°C/min. The response factors for five of the products were determined using pure compounds. The percentage yields of products were determined individually by GC and were calculated based on the starting material. Because a small amount of sample was used in many batch reactions, the recovery of unreacted dibenzothiophene (material balance) was not always satisfactory. Consequently, the conversion was determined based on the yields of recovered reaction products.

Results and Discussion

Reactions at Low Catalyst Loadings. The initial reactions of dibenzothiophene (DBT) were performed using ammonium tetrathiomolybdate (ATTM) and molybdenum hexacarbonyl, $Mo(CO)_6$, as catalyst precursors. The metal loading was 0.5 mol%; when sulfur was added, the sulfur/metal ratio was 4. The solvent was tridecane. The results are summarized in Table 1. At this low loading level, both precursors displayed only moderate catalytic activity. However, when sulfur was added to reactions involving $Mo(CO)_6$, conversion increased significantly.

Comparing first the reactions without added sulfur, the most significant difference lies in the extent of hydrogenation. Desulfurization of dibenzothiophene produces biphenyl. This hydrogenolysis of the C–S bonds, leading to biphenyl, is thought to be the first step in the hydroconversion of dibenzothiophene.[11] Although the amounts of biphenyl produced using the two catalyst precursors appear at first sight to be comparable, ATTM also produces cyclohexylbenzene, which may arise from the hydrogenation of biphenyl. The total desulfurization achieved with ATTM is thus about double that obtained with $Mo(CO)_6$. In addition, significant amounts of tetrahydrodibenzothiophene formed in the reaction over ATTM, with much less being formed in the reaction with $Mo(CO)_6$. In fact, ATTM under these

Table 1. Conversion of Dibenzothiophene in the Presence of Mo-Based Catalyst Precursors (0.5 - 5 mol % metal loading).

Experiment ID	BLDA3/4	BLDM5/6	BLDM12	BLDM10/11	BLDMS1/2	BLDMS5
Catalyst Precursor	ATTM[a]	Mo(CO)$_6$[a]	Mo(CO)$_6$[b]	Mo(CO)$_6$ [5 mol %][a]	S+Mo(CO)$_6$ [4:1][a]	S+Mo(CO)$_6$ [4:1][b]
Conversion (%)[c]	10.4	2.4	4.6	9.3	16.9	14.9
Product (mol %)[d]						
TH-DBT	5.4	0.4	0.8	2.5	7.7	8.0
BP	2.5	1.9	3.0	5.6	3.9	4.3
CHB	1.2	0	0.1	0.4	1.8	2.1
BCH	0	0	0	0	0	0
BNZ	0	0	0	0	0	0
HDS product (mol%)	3.7	1.9	3.1	6.0	5.7	6.3

Solvent: [a]tridecane, [b]octadecane. [c]Conversion is based on the yields of recovered products. [d]Products: biphenyl (BP), tetrahydrodibenzothiophene (TH-DBT), cyclohexylbenzene (CHB), bicyclohexyl (BCH), and benzene (BNZ). HDS product = sum of yields of BP, CHB, BCH, and BNZ.

4B

conditions gives a yield of the product of ring hydrogenation without C–S bond scission (i.e., tetrahydrodibenzothiophene) much higher than the sum of the yields of desulfurization products. (Subsequent desulfurization of the tetrahydrodibenzothiophene could also represent a route to the observed cyclohexylbenzene.) Hydrogenation of benzothiophene can result in rapid formation of hydrogenated products, to the extent that the hydrogenated compounds could be intermediates in the hydrodesulfurization reactions.[12-14] Saturation of a benzene ring neighboring the thiophene ring enhances subsequent C–S bond hydrogenolysis by increasing the electron density on the sulfur atom.[15] With thiophene itself, the ring is not hydrogenated before C–S bond cleavage occurs.[14]

The addition of sulfur to reactions of $Mo(CO)_6$ has a dramatic effect on conversion and on the product slate. Conversion increases by a factor of three or more relative to reaction without added sulfur. In addition, hydrogenated products become of increasing importance. Cyclohexylbenzene occurs among the products, whereas it did not form in reactions without added sulfur. Tetrahydrodibenzothiophene now becomes the dominant product, similar to reactions in the presence of the sulfur-containing precursor ATTM, but was a minor product in reactions without sulfur. Although a greater quantity of products form in reaction with $Mo(CO)_6$ and added sulfur, relative to reactions with ATTM (as indicated by the higher conversion in the former case), the proportions of products are very similar. The ratio of tetrahydrodibenzothiophene to biphenyl, indicating ring hydrogenation vs. hydrodesulfurization, is 2.16 from reaction with ATTM and 1.97 from reaction with $Mo(CO)_6$+S. The ratio of cyclohexylbenzene to biphenyl is 0.48 for the ATTM reaction and 0.46 for $Mo(CO)_6$+S.

Increasing the loading of $Mo(CO)_6$, even without adding sulfur, also increases conversion of dibenzothiophene. With a 5 mol% loading of $Mo(CO)_6$, conversion increased by about a factor of four, from 2.4% to 9.3%. Both desulfurization and ring hydrogenation are enhanced. The tetrahydrodibenzothiophene/biphenyl ratio increases from 0.21 at a 0.5 mol% loading to 0.45 with the 5 mol% loading. The ratio of cyclohexylbenzene to biphenyl, which was zero in the reaction with 0.5 mol% loading, rises to 0.07 when 5 mol% loading is used.

Our results with $Mo(CO)_6$ at 0.5 or 5 mol% loadings differ from earlier work using supported catalysts made from molybdenum carbonyl complexes. In that work,[16] hydrogenation produced some bicyclohexyl, which we did not observe at 0.5 or 5 mol% loadings (but see further discussion below). Sulfiding the catalyst resulted in low activity, with conversions of dibenzothiophene of about 26%.[16] On the other hand, the addition of sulfur to molybdenum naphthenates enhances hydrogenation and hydrodesulfurization (relative to reaction without sulfur) of dibenzothiophene.[17] In that case, hydrogenation products included both cyclohexylbenzene and bicyclohexyl.[17]

It has been reported that hydrogen sulfide inhibits hydrogenation reactions of dibenzothiophene and related compounds.[11,13,14,18,19] We saw no evidence of such inhibition in

the reactions just discussed, nor in reactions to be mentioned below, that involved sulfur/metal ratios of 6, where significant production of H_2S might be expected. Gates discusses the change in selectivity, with selectivity for C–S bond hydrogenolysis relative to hydrogenation reactions decreasing with increasing partial pressure of H_2S in the reactor.[20] Our results with ATTM and $Mo(CO)_6$+S on the one hand vs $Mo(CO)_6$ on the other agree with this.

We also investigated the effect of changing the solvent from tridecane to the higher boiling octadecane. When $Mo(CO)_6$ is used as the precursor, the change to higher boiling solvent increases conversion and shows a slight tendency to enhance hydrogenation. The ratio of tetrahydrodibenzothiophene to biphenyl rises from 0.21 to 0.27. A small yield of cyclohexylbenzene, not observed in reaction in tridecane, appears in the reaction in octadecane. The higher boiling solvent provides a greater amount of liquid phase. Hydrogenation of dibenzothiophene is enhanced when reaction occurs in the liquid phase.[21] For reactions using $Mo(CO)_6$ with added sulfur, the change of solvent has little impact on product distribution.

Reactions at High Catalyst Loadings. We noted above that an increase in loading of $Mo(CO)_6$ from 0.5 to 5 mol% had a significant effect on conversion. That observation led us to examine the reactions of dibenzothiophene at much higher catalyst loading, specifically 36 mol%. The results of these reactions are shown in Table 2. There are some unidentified products which are not reported in Table 2. One in particular has a mass of 166 daltons; we have tentatively identified it as cyclopentylmethylcyclohexane.

For reactions with ATTM, the increase in loading to 36 mol% increases conversion, substantially increases hydrogenation, and results in some hydrocracking. Some of the effects of increased conversion in ATTM systems are summarized in Figure 1. Several factors highlight the increased hydrogenation. Compared to reaction with 0.5 mol% loading and tridecane solvent, the tetrahydrodibenzothiophene/biphenyl ratio has dropped from 2.16 to 0.52. At the same time, the ratio of cyclohexylbenzene to biphenyl has increased from 0.48 to 1.83. A small but noticeable yield of benzene signals the onset of hydrocracking reactions. Molybdenum sulfides can catalyze C–C bond cleavage as well as hydrogenation reactions.[22] In our case the hydrocracking reaction may be facilitated by the products being confined in a closed batch reactor. No evidence for C–C bond scission in dibenzothiophene hydrogenation was observed in a flow reactor at high space velocities.[12] Similar to the results discussed above for $Mo(CO)_6$ at 0.5 mol% loading, a change to higher boiling solvent with ATTM at 36 mol% loading also shows increased conversion and enhanced hydrogenation. Conversion nearly doubles, from 32.2 to 60.3%, with change of solvent from tridecane to octadecane. Yields of tetrahydrodibenzothiophene and cyclohexylbenzene increase. Hydrocracking, for which there was no evidence in any of the reactions at loadings ≤5 mol%, decreases in importance with the switch to higher-boiling solvent. In tridecane, the ratio of benzene to biphenyl was 0.55, but this value drops to 0.32 when octadecane is used as the

Table 2. Conversion of Dibenzothiophene in the Presence of Mo-Based Catalyst Precursors (36 mol % metal loading).

Experiment ID	BCDA5	BCDA4	BCDM1/2	BCDM5/6	BCDMS1/2	BCDMS5/6	BCDMS7	BCDMS8
Catalyst Precursor	ATTM[a]	ATTM[b]	$Mo(CO)_6$[a]	$Mo(CO)_6$[b]	S + $Mo(CO)_6$ [6:1][a]	S + $Mo(CO)_6$ [2:1][c]	S + $Mo(CO)_6$ [6:1][c]	S + $Mo(CO)_6$ [6:1][b]
Conversion (%)	32.2	60.3	53.2	77.2	74.4	96.2	100.0	100.0
Products (mol %)								
TH-DBT	3.3	4.7	2.1	2.1	3.0	0	0	0
BP	6.4	11.4	39.1	48.3	12.0	9.9	2.6	0
CHB	11.7	17.7	8.5	14.1	19.7	20.7	23.0	19.1
BCH	3.2	3.2	0	14.6	3.9	2.5	4.7	11.0
BNZ	3.5	3.7	3.2	3.0	11.1	15.8	10.9	13.8
HDS Product (mol%)	24.8	36	50.8	80.0	46.7	48.9	41.2	43.9

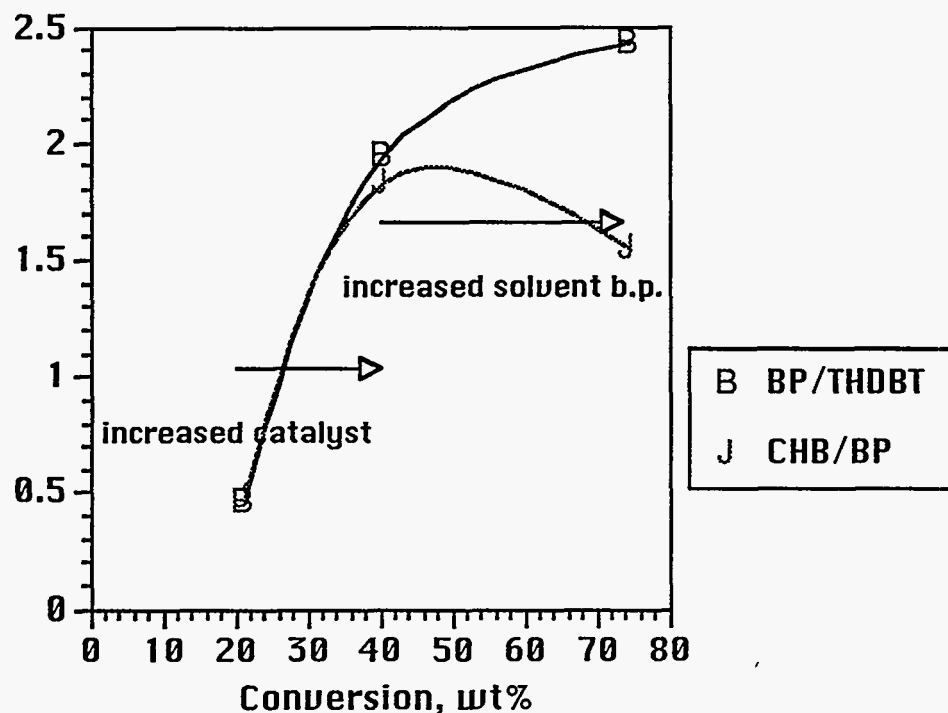Solvent: [a]tridecane, [b]octadecane, [c]heptadecane.

solvent.

Figure 1. Relative significance of hydrodesulfurization and hydrogenation, and enhancement of secondary hydrogenation reactions, as dibenzothiophene conversion increases in ATTM-catalyzed reactions. Here BP = biphenyl, THDBT = tetrahydrodibenzothiophene, and CHB = cyclohexylbenzene.

For $Mo(CO)_6$ in tridecane, an increase in catalyst loading from 0.5 to 36 mol% provides an order-of-magnitude increase in conversion. At 0.5 mol% loading, ATTM gives higher values of both tetrahydrodibenzothiophene/biphenyl and cyclohexylbenzene/ biphenyl ratios than are obtained with $Mo(CO)_6$. The same behavior is seen at this much higher catalyst loading. In fact, the ten-fold difference in the former ratio between ATTM and $Mo(CO)_6$ at 0.5 mol% loading occurs again at 36 mol% loading. As with ATTM, this higher loading of $Mo(CO)_6$ shows some evidence of hydrocracking, as indicated by the occurrence of benzene among the reaction products. As also observed with lower catalyst loadings, a change from tridecane to octadecane as solvent increases conversion and extent of hydrogenation among the products. Ishihara and Kabe[23,24] also observed solvent effects in the reaction of DBT over a commercial sulfided Co-Mo/Al_2O_3 catalyst, where it was found the catalytic activity decreased in the following order: n-heptane > xylene > decalin > tetralin. As can be seen from Table 2, with $Mo(CO)_6$ in octadecane,

the increased hydrogenation is particularly evident with significant yield of the fully hydrogenated bicyclohexyl.

At 0.5 mol% catalyst loading, the addition of sulfur along with $Mo(CO)_6$ increased conversion and extent of hydrogenation. A generally similar effect occurs at the 36 mol% loading. For example, in tridecane the conversion rises, with added sulfur, from 53.2 to 74.4% and the contribution of cyclohexylbenzene to the product slate rises from 8.5 to 19.7 mol%. However, a particularly noteworthy feature of the addition of sulfur at these high catalyst loadings is the remarkable increase in hydrocracking, with benzene now becoming one of the products in highest concentration. In octadecane, the addition of sulfur, albeit at a sulfur/metal ratio of 6, increases conversion from 77.2 to 100%, and so greatly increases hydrogenation and hydrocracking that the observed products no longer even contain biphenyl. Rather, they are the "second generation" of products: cyclohexylbenzene, bicyclohexyl, and benzene. There are other hydrocracking products which are not listed in Table 2.

We also investigated molybdenum(III) chloride as a catalyst precursor at the 36 mol% loading. Results are provided in Table 3. In tridecane, and without added sulfur, the conversion is comparable to that obtained with $Mo(CO)_6$, 46.0 vs. 53.2%. The significant difference, however, lies in the nature of the products. No hydrogenated products formed in the reaction with $MoCl_3$, and the extent of hydrocracking to benzene was increased. The increased hydrocracking, relative to reaction with $Mo(CO)_6$, can be explained by the acidity of $MoCl_3$. The acidity and hydrocracking ability of $MoCl_3$ have been discussed elsewhere.[25] When using supported catalysts for hydroprocessing, the extent of hydrocracking is enhanced as the acidity (in this case, of the support) is increased.[3] As with the other catalyst precursors, a change to the higher boiling solvent increased conversion, though not so much as with ATTM or $Mo(CO)_6$, and provided some amount of hydrogenation, as seen in the small yields of tetrahydrodibenzothiophene and cyclohexylbenzene.

The effect of sulfur addition on conversions obtained with $MoCl_3$ differs greatly from reactions with $Mo(CO)_6$. Regardless of the solvent used, addition of sulfur decreases conversion relative to reactions in the same solvent without sulfur. The $MoCl_3+S$ reactions resemble $Mo(CO)_6+S$ reactions in that sulfur addition increases the contribution of hydrogenated products to the product slate (as can be seen, for example, in the considerably greater yield of cyclohexylbenzene in octadecane), and diminishes the effect of changing solvent.

The above results suggest that dispersed catalysts can promote hydrodesulfurization of dibenzothiophene through two pathways shown in Scheme 1; one via direct C-S bond hydrogenolysis (path I) and the other via hydrogenation of a benzene ring neighboring the thiophene ring (path II). The type of Mo-containing precursors, sulfur addition and solvent type affect the catalytic activity and the relative contribution of path I and path II to hydrodesulfurization. Despite the fact that we used catalyst precursors at 36 mol% loading with

Table 3. Conversion of Dibenzothiophene in the Presence of Mo-, Fe, and Co-Based Catalyst Precursors [36 mol % metal loading].

| Experiment ID	BCDT3	BCDT2	BCDTS3	BCDTS2	BCDC2	BCDMC1	BCDF1	BCDFS1
Catalyst Precursor	MoCl$_3$[a]	MoCl$_3$[b]	S + MoCl$_3$ [6:1][a]	S + MoCl$_3$ [6:1][b]	Co$_2$(CO)$_8$[b]	MoCo-TC2[b]	Fe(CO)$_5$[b]	S + Fe(CO)$_5$ [6:1][b]
Conversion (%)	46.0	66.4	37.9	41.6	28.7	21.0	14.4	19.6
Products (mol %)								
TH-DBT	0	6.9	4.1	4.5	0	2.5	0	0
BP	33.3	42.5	11.3	12.0	5.6	7.0	4.4 .	4.5
CHB	0	2.3	2.8	11.5	13.1	11.5	10.0	15.1
BCH	0	0	0	3.8	13.1	0	0	0
BNZ	7.0	13.2	7.4	5.0	0	0	0	0
HDS product (mol%)	40.3	58.0	21.5	32.3	31.8	18.5	14.4	19.6

Solvent: [a]tridecane, [b]octadecane.

added sulfur, we observed the same products as those observed by Ishihara and Kabe[23,24] in hydrodesulfurization of DBT using supported catalysts including a sulfided commercial Co-Mo/Al$_2$O$_3$ catalyst[23] and a Mo(CO)$_6$/SiO$_2$-Al$_2$O$_3$ catalyst.[24]
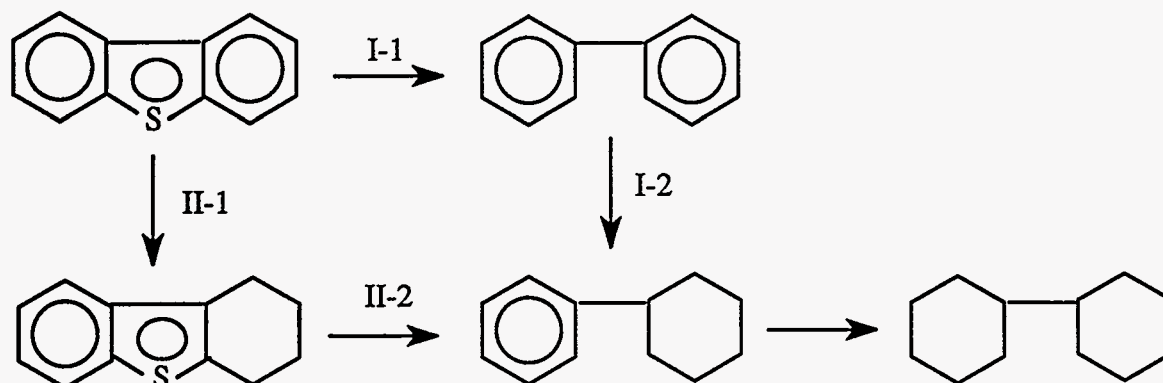
Scheme 1. Possible reaction pathways for hydrodesulfurization of dibenzothiophene

In the absence of sulfur, Mo(CO)$_6$ or its decomposition products Mo(CO)$_x$ may react with DBT or its products to form MoS$_2$. The data in Table 2 (higher biphenyl yield with 36 mol% Mo(CO)$_6$ without sulfur) seem to support this consideration, but such reaction is unlikely in the presence of added sulfur. It should also be mentioned that the amount of DBT used for runs with 36 mol% metal loading is close to the sulfur concentration in coal liquefaction reaction system except that coal was not used; in these runs the seemingly very high metal loading is due in part to the low sulfur concentration (1 wt% DBT in the reaction solvent).

Reactions with Cobalt-Molybdenum Thiocubane. The promoting effect of cobalt on molybdenum-based hydrotreating catalysts is well known.[3,11,13,20] Mixed cobalt-molybdenum sulfides provide good hydrodesulfurization activity.[26] For monometallic catalysts, the active sulfide phases are Co$_9$S$_8$ and MoS$_2$. In some cases even a simple physical mixture of these compounds shows increased catalytic activity relative to MoS$_2$.[14,27] Good results have also been obtained by treating ATTM with cobalt nitrate.[28] We discussed previously the interesting work of Topsøe and his group that culminated in the suggestion that Co-Mo bond distances in the active phase in sulfided cobalt-molybdenum catalysts are similar to those seen in some cobalt-molybdenum cluster compounds.[6-8] Therefore we were interested to examine the behavior of the thiocubane complex Cp$_2$Co$_2$Mo$_2$(CO)$_2$S$_4$, whose structure is given in Scheme II.
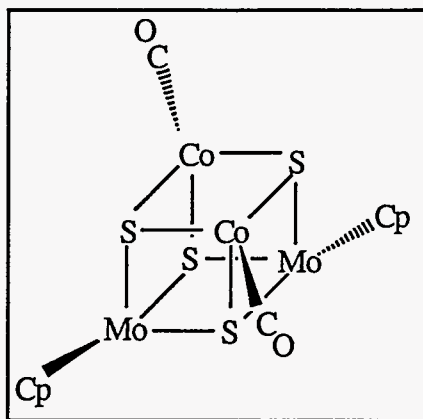
Scheme 2. Structure of the thiocubane cluster $Cp_2Co_2Mo_2(CO)_2S_4$.

The results with this bimetallic thiocubane (MoCo-TC2) are shown in Table 3. Remarkably, particularly in light of the known promoting ability of cobalt, the conversion is very low, only 21.0%. The dominant product, however, is both desulfurized and hydrogenated— cyclohexylbenzene. The hydrogenation accompanying reaction differs from some results obtained by Vrinat, who saw hydrogenated dibenzothiophenes formed over supported molybdenum but not over cobalt-molybdenum catalysts.[29]

At present we cannot explain the poor performance of this catalyst precursor. We have not yet determined the structure of the catalytically active phase. That information may provide clues to explain the unexpectedly low conversion obtained. For example, among the unusual Chevrel-phase catalysts (compounds of general formula $M_xMo_6Z_8$, where Z is one of the chalcogens and M can be, among many other elements, cobalt[30]) the cobalt-containing compounds are the least active for hydrogenation.[31]

Comparative Behavior of Selected Metal Carbonyls. We have discussed above the good performance obtained from using $Mo(CO)_6$, with and without sulfur, particularly at 36 mol% loading in octadecane. This behavior sparked interest in examining other carbonyls, in particular dicobalt octacarbonyl, $Co_2(CO)_8$, and iron pentacarbonyl, $Fe(CO)_5$. Results are provided in Table 3. Neither cobalt nor iron carbonyl gives satisfactory performance compared to Mo-based catalysts. Conversions are less than 30%, indeed less than 20% for iron carbonyl, even with added sulfur. No hydrocracking is evident.

The details of the active species of the in situ generated dispersed catalysts are not yet established. In the presence of added sulfur, the catalytically active species are believed to be

metal sulfides.[32]   It is commonly held that the active species of molybdenum under hydrotreating conditions are molybdenum sulfides close to MoS_2 in stoichometry. Earlier work[33] showed that the oxide form and sulfided form of a commercial supported $Ni-Mo/Al_2O_3$ catalyst are equally effective for hydrogenation of phenanthrene and anthracene, but the sulfided form is more active for coal liquids upgrading and for reactions involving heteroatoms.   For MoS_2 catalyst, a recent model proposed by Daage and Chianelli[34,35] indicates that hydrogenation reaction is catalyzed predominately by rim sites for large molecules like DBT; sulfur removal is catalyzed by edge sites. For iron sulfide, it is believed that pyrrhotite ($Fe_{1-x}S$) is the catalytically active form, and pyrrhotite can be formed from $Fe(CO)_5$ and sulfur.[36]

Summary and Conclusions

Dibenzothiophene was relatively stable in non-catalytic reactions. At the conditions used here, 400°C, 30 min., non-donor solvent, and 6.9 MPa (cold) hydrogen pressure, it reacts only with very active catalysts and high metal loadings to form hydrodesulfurized products. In reactions with ATTM and molybdenum hexacarbonyl at 0.5 mol% metal loading, with and without added sulfur, only low catalytic activity could be observed. The product distribution from reactions at this low metal loading showed only hydrogenation products. $Mo(CO)_6$ at 36 wt% metal loading, with added sulfur in a 6:1 S:Mo ratio and octadecane solvent, was the most active catalyst, yielding 100% hydrodesulfurization and conversion. ATTM and molybdenum(III) chloride are less active for hydrodesulfurization under similar conditions. The other catalyst precursors, $Co_2(CO)_8$, $Fe(CO)_5$, and $Cp_2Co_2Mo_2(CO)_2S_4$, showed little activity.

Using a high boiling solvent is beneficial to hydrodesulfurization, conversion, and the formation of hydrogenated products. Sulfur addition generally enhances conversion, though not in the specific case of $MoCl_3$. The dominant products in the product slate are clearly determined by the reaction conditions; for example, sulfur addition generally shifts products toward hydrogenation and hydrocracking.

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