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Novel Bimetallic Dispersed Catalysts for Temperature-Programmed Coal Liquefaction

Final Report

**Chunshan Song, Harold H. Schobert, Derrick P. Parfitt, Eckhardt
Schmidt, Stephen Kirby, Shona Martin, Yoshiharu Yoneyama, Boli
Wei, M. Madhusudan Reddy, and William S. Cooke**

**Fuel Science Program and
Laboratory for Hydrocarbon Process Chemistry
The Pennsylvania State University
University Park, Pennsylvania 16802-2303**

November 1997

**Prepared for the U.S. Department of Energy
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ABSTRACT

It is an indisputable fact that the world will continue to rely heavily on liquid hydrocarbon fuels for transportation. Petroleum is the only dominant source of liquid fuels in the developed countries. Coal-derived liquids through coal liquefaction have been identified as a prospective alternative transportation fuel in the future. It seems likely that at some point in the 21st century the supply of petroleum will have declined to a level that makes synthetic liquid fuels from coal a viable option. Development of new catalysts is a promising approach to more efficient coal liquefaction. It has been recognized that dispersed catalysts are superior to supported catalysts for primary liquefaction of coals, because the control of initial coal dissolution or depolymerization requires intimate contact between the catalyst and coal. This research is a fundamental and exploratory study on catalytic coal liquefaction, with the emphasis on exploring novel bimetallic dispersed catalysts for coal liquefaction and the effectiveness of temperature-programmed liquefaction using dispersed catalysts.

The primary objective of this research was to explore novel bimetallic dispersed catalysts from organometallic molecular precursors, that could be used in low concentrations but exhibit relatively high activity for efficient hydrol liquefaction of coals under temperature-programmed conditions. We have synthesized and tested various catalyst precursors in liquefaction of subbituminous and bituminous coals and in model compound studies to examine how do the composition and structure of the catalytic precursors affect their effectiveness for coal liquefaction under different reaction conditions, and how do these factors affect their catalytic functions for hydrogenation of polyaromatic hydrocarbons, for cleavage of C-C bonds in polycyclic systems such as 4-(1-naphthylmethyl)biphenyl, for hydrogenolysis of C-O bond such as that in dinaphthylether, for hydrodeoxygenation of phenolic compounds and other oxygen-containing compounds such as xanthene, and for hydrodesulfurization of polycyclic sulfur compounds such as dibenzothiophene.

The novel bimetallic and monometallic precursors synthesized and tested in this project include various Mo- and Fe-based compounds. Examples of such Mo-based bimetallic complexes that contain Mo, Co, and S in a single molecule include bimetallic thiocubanes: $\text{Mo}_2\text{Co}_2\text{S}_4(\text{S}_2\text{CNEt}_2)_2(\text{CH}_3\text{CN})_2(\text{CO})_2$ [designated as MoCo-TC1], $\text{Mo}_2\text{Co}_2\text{S}_4\text{Cp}_2(\text{CO})_2$ [MoCo-TC2], and $\text{Mo}_2\text{Co}_2\text{S}_4(\text{Cp}')_2(\text{CO})_2$ [MoCo-TC3], in which Et, Cp and Cp' represent ethyl, cyclopentadiene, and pentamethylcyclopentadiene, respectively, and the trianionic bimetallic complex, $(\text{PPh}_4)_3\text{Co}(\text{MoS}_4)_2$, which is designated as MoCo-S. Examples of such Fe-based precursors include a cyclopentadienyliron dicarbonyl dimer $\text{Cp}_2\text{Fe}_2(\text{CO})_4$, a thiocubane type

cluster $\text{Cp}_4\text{Fe}_4\text{S}_4$, a series of carbonyl precursors including $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, and $\text{Fe}_3(\text{CO})_{12}$, and superfine iron oxide with average particle size of 30 Å (SFIO).

Many interesting and stimulating results have been obtained from this experimental study, and they are highlighted in the Executive Summary section of this report and discussed in detail in individual sections in the 11 chapters of this report. As but one example, the bimetallic catalyst generated in-situ from MoCo-TC2 has been found to be substantially more active than those from mixed metal carbonyls and the mixture of $\text{Mo}(\text{CO})_6 + \text{Co}_2(\text{CO})_8$ plus sulfur for liquefaction of a Montana subbituminous coal (DECS-9) at the loading level of 0.5 wt% Mo on dmmf coal. The performance of the Mo-Co bimetallic catalyst was further enhanced by using temperature programmed liquefaction (TPL) conditions consisting of a low temperature soaking at 200°C, programmed heat-up to 400 or 425°C followed by a 30 minutes hold. The programmed heat-up serves as an in-situ activation of catalyst and coal pretreatment, which contributes to more effective hydrogenation of reactive fragments at high temperature. The method of dispersion and the impregnating solvent also affect the catalytic activity significantly. Impregnating MoCo-TC2 onto coal from a swelling solvent system, a mixture of toluene-tetrahydrofuran (THF), affords the highest conversion (92 wt%) and highest oil yield for runs at 400 °C under TPL conditions. These results indicate that proper binding of Mo, Co, and S in a single molecule could result in a bimetallic sulfide catalyst that has much higher activity than the corresponding mixtures of the Mo and Co compounds plus sulfur, and that the performance of better catalysts can be further improved by using proper operation conditions. Another example is hydrogenolysis and hydrodeoxygenation reactions of selected oxygen compounds including anthrone (carbonyl), dinaphthyl ether (aryl-aryl ether), xanthene (heterocyclic ether), and 2,6-di-*t*-butyl-4-methylphenol (hydroxyl) at 300°C, 350°C and 400°C for 30 minutes under 1000 psig H_2 . The reactivity order of the oxygen functionalities in the presence of the various catalysts is different. For non-catalytic conditions the order appears to be : carbonyl > aryl-aryl ether » substituted phenol ≈ heterocyclic ether. For reactions involving MoCo-TC2 the reactivity order appears to be : carbonyl > aryl-aryl ether > heterocyclic ether > substituted phenol, and with monometallic ATTM this sequence changes to: carbonyl > substituted phenol ≈ aryl-aryl ether » heterocyclic ether.

It should be mentioned that, because of the structural complexity of coal, the results from coal liquefaction can not be interpreted at the molecular level. In this context, the model compound results from this study need to be viewed carefully as model reactions, not as coal conversion. In this project, all the catalytic tests were conducted in small batch reactors of <40 mL volume. The results are internally comparable, but care should be taken when comparing the results from such small-scale laboratory tests with those from large reactors or pilot plant tests.

EXECUTIVE SUMMARY OF MAJOR FINDINGS

The primary objective of this research was to explore novel bimetallic dispersed catalysts from organometallic molecular precursors, that can be used in low concentrations but exhibit relatively high activity for efficient hydroliquefaction of coals. We have prepared and tested various heteronuclear (and homonuclear) organometallic molecules with known or desired structure as catalyst precursors that contain covalently bound, two different metal atoms and sulfur in a single molecule. Such precursors are expected to generate finely dispersed bimetallic catalysts such as Co-Mo and Ni-Mo binary sulfides upon thermal decomposition under coal liquefaction conditions. Concordant with the goal of exploring new catalysts for liquefaction process, we sought to understand the functions of the new catalysts and their effects on product quality by performing model reactions of aromatic and polar compounds that are relevant to coal liquefaction and by analyzing the products from coal liquefaction. At the onset of this project, the status of coal liquefaction research and development and the need to explore bimetallic or multi-component catalysts were summarized in an excellent review by Derbyshire (1988). A good review on the German roots of conversion of coal into liquid fuels was published by Stranges (1987).

This report is a summary of the major results from our experimental research, consisting of 11 chapters. Chapter 1 describes the synthetic preparation of organometallic bimetallic compounds as catalyst precursors containing Mo, Co and S. In the initial work, we synthesized several bimetallic complexes that contain Mo, Co, and S in a single molecule. Three of them are bimetallic thiocubanes: $\text{Mo}_2\text{Co}_2\text{S}_4(\text{S}_2\text{CNEt}_2)_2(\text{CH}_3\text{CN})_2(\text{CO})_2$ [designated as MoCo-TC1], $\text{Mo}_2\text{Co}_2\text{S}_4\text{Cp}_2(\text{CO})_2$ [MoCo-TC2], and $\text{Mo}_2\text{Co}_2\text{S}_4(\text{Cp}')_2(\text{CO})_2$ [MoCo-TC3], in which Et, Cp and Cp' represent ethyl, cyclopentadiene, and pentamethylcyclopentadiene, respectively. These thiocubanes were synthesized in our laboratory based on the procedures reported in literature. For comparative examination, the trianionic bimetallic complex, $(\text{PPh}_4)_3\text{Co}(\text{MoS}_4)_2$, was also synthesized. This bimetallic sulfide complex contains cobalt bis-tetrathiomolybdate trianion, $\text{Co}(\text{MoS}_4)_2^{3-}$, and is designated as MoCo-S.

Chapter 2 reports on the catalytic performance of several heterometallic complexes consisting of two transition metals, Mo and Co, and sulfur in a single molecule as precursors of bimetallic dispersed catalysts for liquefaction of a Montana subbituminous coal (DECS-9) at the loading level of 0.5 wt% Mo on dmmf coal. It was found that the structure of the precursors, in particular the ligands to the metal species, affect the activity of the resulting catalyst significantly.

Among the M-M' type precursors tested, Mo-Co thiocubane, $\text{Mo}_2\text{Co}_2\text{S}_4(\text{Cp})_2(\text{CO})_2$ [Cp = cyclopentadiene], designated as MoCo-TC2, produced in-situ the best catalyst.

The performance of the Mo-Co bimetallic catalyst was further enhanced by using temperature programmed (TPL) conditions consisting of a low temperature soaking at 200°C, programmed heat-up to 400 or 425°C followed by a 30 minutes hold. The programmed heat-up serves as an in-situ activation of catalyst and coal pretreatment, which contributes to more effective hydrogenation of reactive fragments at high temperature. The method of dispersion and the impregnating solvent also affect the catalytic activity significantly. Impregnating MoCo-TC2 onto coal from a swelling solvent system, a mixture of toluene-tetrahydrofuran (THF), affords the highest conversion (92 wt%) and highest oil yield for runs at 400 °C under TPL conditions.

The bimetallic catalyst generated in-situ from MoCo-TC2 is substantially more active than those from mixed metal carbonyls and the mixture of $\text{Mo}(\text{CO})_6 + \text{Co}_2(\text{CO})_8$ plus sulfur. These results indicate that proper binding of Mo, Co, and S in a single molecule could result in a bimetallic sulfide catalyst that has much higher activity than the corresponding mixtures of the Mo and Co compounds plus sulfur.

Chapter 3 deals with model hydrocracking reactions of 4-(1-naphthylmethyl)bibenzyl over Mo- and Co-based monometallic and bimetallic dispersed catalysts. Coal liquefaction involves cleavage of methylene and dimethylene bridges connecting polycyclic aromatic units. The selected compound for model coal liquefaction reactions is 4-(1-naphthylmethyl)bibenzyl, abbreviated as NMBB. This chapter describes the synthesis and screening of several hetero- and homometallic complexes as precursors of dispersed catalysts for hydrocracking of NMBB. Experiments were carried out at 400 °C for 30 min under 6.9 MPa H_2 pressure.

$(\text{NH}_4)_2\text{MoS}_4$ and MoCl_3 converted NMBB predominately into naphthalene and 4-methylbibenzyl. Small amounts of secondary products were formed by hydrogenation and fragmentation of the primary products. Lewis acid-type MoCl_3 catalyst gave lower selectivity to the primary products, with relatively larger amounts of methyltetrahydronaphthalene- and methyl-naphthalene-derivatives. In contrast, the bimetallic catalyst precursors $\text{Cp}_2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_4$ and $(\text{Ph}_4\text{P})_2(\text{Ni}(\text{MoS}_4))$ inflict less fragmentation and less hydrogenation of primary cleavage products. $\text{Cp}_2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_4$ converted a substantial amount of starting material even at 350 °C; whereas, a noncatalytic run under the same conditions showed only small conversion. Inorganic and bimetallic catalyst precursors gave similar conversions.

Greater product selectivity can be achieved by means of organometallic precursors and low severity reaction conditions. $\text{Mo}(\text{CO})_6$ and $\text{Co}_2(\text{CO})_8/\text{Mo}(\text{CO})_6$ gave similar conversion as the

bimetallic catalyst precursors. The addition of sulfur to the combination $\text{Co}_2(\text{CO})_8/\text{Mo}(\text{CO})_6$ gave significantly higher conversion but reduced generally the yield of hydrogenation products.

Chapter 4 is concerned with the catalytic activity of three different types of catalyst precursors in model hydrogenation reactions of phenanthrene. The first catalyst is a heterometallic complex consisting of two transition metals, Mo and Ni, and sulfur in a single molecule, $[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{Ni}(\text{MoS}_4)_2]$. This Ni-Mo complex consists of the dianion $[\text{Ni}(\text{MoS}_4)_2]^{2-}$ core unit and tetraphenylphosphonium as counter ion. The second is a thiocubane type complex consisting of cobalt, molybdenum and sulfur, which is the MoCo-TC2 described in Chapters 1-3. The third is a thiocubane type cluster consisting of iron and sulfur, $[\text{C}_5\text{H}_5\text{FeS}_4]_4$ (referred to as Fe4) and the fourth, the pure inorganic salt ammonium tetrathiomolybdate (ATTM). It was found that the structure and the ligands in the model complexes affect the activity of the resulting catalyst significantly. The optimum reaction conditions at a pressure of 6.9 MPa hydrogen gas varied for different catalysts. The bimetallic catalysts generated in situ from the organometallic precursor are more active than monometallic catalysts like ATTM and the thiocubane type cluster Fe4. Main products are hydrogenated phenanthrene derivatives, like DHP, THP, sym-OHP, cis- and trans-sym-OHP with minor isomerization products such as sym-OHA. Our results indicate that other transition metal and ligand combinations in the organometallic precursors and the use of another model compound could result in substantially higher conversion activity.

Chapter 5 describes the catalytic activity of iron thiocubane and inorganic Fe compounds as catalyst precursors for hydrocracking of 4-(1-naphthylmethyl)bibenzyl (NMBB). Catalytic hydrocracking of NMBB predominantly yielded naphthalene and 4-methylbibenzyl. Various iron compounds were examined as catalyst precursors. Sulfur addition to most catalyst precursors led to substantially higher catalyst activity and higher conversion. NMBB was also treated with sulfur in the absence of iron compounds, in concentrations of 1.2–3.4 wt%, corresponding to the conditions present in reactions with added iron compounds. Increasing sulfur concentrations led to higher NMBB conversions. Furthermore, sulfur had a permanent effect on the reactor walls. A black sulfide layer formed on the surface which could not be removed mechanically. The supposed non-catalytic reactions done in the same reactor but after experiments with added sulfur showed higher conversions than comparable experiments done in new reactors. This wall catalytic effect can be reduced by treating the sulfided reactors with hydrochloric acid. The results of this work demonstrate the significant effect of sulfur addition and sulfur-induced residual wall effects on carbon-carbon bond cleavage and hydrogenation of aromatics.

Chapter 6 describes activity of Fe catalysts derived in situ from various organometallic Fe precursor compounds with and without sulfur for hydrocracking of 4-(1-naphthylmethyl)bibenzyl,

NMBB. The first aim is to examine the relationship between the structure of catalyst precursor molecules and the catalytic activity and selectivity of the dispersed Fe catalysts generated in situ; the second aim is to develop an basic understanding of catalytic reaction chemistry involving the C-C bond cleavage and aromatics hydrogenation, using 4-(1-naphthylmethyl)bibenzyl.

We have examined a cyclopentadienyliron dicarbonyl dimer $\text{Cp}_2\text{Fe}_2(\text{CO})_4$, a thiocubane type cluster $\text{Cp}_4\text{Fe}_4\text{S}_4$, a series of carbonyl precursors including $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, and $\text{Fe}_3(\text{CO})_{12}$, and superfine iron oxide with average particle size of 30 Å (SFIO). The results with the above precursors revealed several interesting trends. First, even the catalysts without sulfur can display certain activity. The particles from $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ showed the highest activity among all the precursors examined. The activity of catalysts from Fe carbonyls decreased with increasing number of irons in the carbonyl compounds: $\text{Fe}(\text{CO})_5 > \text{Fe}_2(\text{CO})_9 > \text{Fe}_3(\text{CO})_{12}$. We also examined the effect of sulfur addition. With one exception, adding sulfur to all the reactions increased NMBB conversion, but decreased yields of hydrogenation products. Another interesting trend is that the activity levels of catalysts from Fe carbonyls rank the same both with and without the S addition. We subsequently examined a S-containing precursor, $\text{Cp}_4\text{Fe}_4\text{S}_4$. Surprisingly, it exhibited the lowest activity, although it has a S-to-Fe ratio closest to pyrrhotite (Fe_{1-x}S , where $x = 0$ to 0.12) which is thought to be the active phase. However, the selectivity for the α -cleavage of the C-C bond in NMBB is the highest with $\text{Cp}_4\text{Fe}_4\text{S}_4$. The nano-scale SFIO particles performed at an activity level similar to that of $\text{Fe}_2(\text{CO})_9$ in the absence of sulfur, but afforded the highest NMBB conversion when S was added.

Based on the product distribution, we can define two main reaction pathways for NMBB over Fe catalysts: one is α -cleavage (path I) and the other is hydrogenation to form THNMBB (path II). Probably these two pathways start from the same intermediate, the radical formed after hydrogen atom attack on ipso position on naphthalene ring. The path I is favored by β -cleavage of the radical intermediate, but path II is favored when the radical intermediate abstracts another hydrogen. They compete with each other. The structure of catalyst precursors and the sulfur addition affect the reaction pathways on the surface of in situ generated catalysts, and such information can be used to guide further research on the catalysis.

In Chapter 7, the catalytic effects of several Mo-, Co-, and Fe-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.

Chapter 8 discusses hydrogenolysis and hydrodeoxygenation reactions of oxygen compounds in coal Liquefaction systems using novel organometallic catalyst precursors. Oxygen-containing functional groups are present in virtually all lignites, subbituminous, and bituminous coals. For hydrodeoxygenation, model compound studies were performed using multi-ring systems, or those of comparable molecular weight, to investigate the capabilities of the dispersed catalysts. The catalyst precursors used were $(\text{NH}_4)_2\text{MoS}_4$ (ATTM), $[\text{Ph}_4\text{P}]_2[\text{Ni}(\text{MoS}_4)_2]$ (Ni-Mo1) and $\text{Cp}_2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_4$ (CoMo-T2, also referred to as MoCo-TC2). Model compound studies were performed to investigate the capabilities of these catalyst precursors. The model compounds selected represent a variety of oxygen functionalities, possibly present in coals of differing ranks. They include anthrone (carbonyl); dinaphthyl ether (aryl-aryl ether); xanthene (heterocyclic ether); and 2,6-di-*t*-butyl-4-methylphenol (hydroxyl). Reactions were performed in a 22ml capacity microreactor (with 0.5 g model compound under 1000 psig H_2) at 300°C, 350°C and 400°C for 30 minutes.

The reactions of these compounds in the presence of several catalyst precursors under liquefaction conditions give an indication of the hydrodeoxygenating abilities of these precursors. From the non-catalytic data obtained there is a clear order of starting material reactivity : 2,6-di-*t*-butyl-4-methylphenol > anthrone > dinaphthyl ether > xanthene. However, the reactivity order of the oxygen functionalities in the presence of the various catalysts is different. For non-catalytic conditions the order appears to be : carbonyl > aryl-aryl ether » substituted phenol ≈ heterocyclic ether. In the presence of ATTM this sequence changes slightly to : carbonyl > substituted phenol ≈ aryl-aryl ether » heterocyclic ether and for reactions involving CoMo-T2 the reactivity order appears to be : carbonyl > aryl-aryl ether > heterocyclic ether > substituted phenol.

These differences in reactivity order emphasize the effect of the nature of the oxygen functionality on the deoxygenating capabilities of the catalysts and that different catalysts can have different roles in promoting hydrodeoxygenation and reduction, depending on the nature of the

starting material. They also highlight the undesirability of phenolic and heterocyclic ether structures in liquefaction systems. Both these structures types are quite unreactive under liquefaction conditions and any reaction has a tendency to form high yields of single-ring phenols.

Liquefaction studies were then performed on a selection of coals of varying rank and oxygen content. Here we report an investigation of the effect a bimetallic organometallic precursor (CoMo-T2) on conversion and product distribution of these coals under liquefaction conditions. For comparison we have conducted the same reactions under non-catalytic conditions, and in the presence of ATTM, commonly used in liquefaction research. Model compound studies indicated that different oxygen functional groups will react differently under liquefaction conditions. The catalyst precursors under investigation facilitate deoxygenation of some model compounds to a greater extent than others. ATTM showed a preference toward phenolic oxygen removal, whereas CoMo-T2 demonstrated greater facilitation of ether cleavage. It was predicted from the model compound results that ATTM should improve the product quality of coals with high phenol contents, by phenolic oxygen removal, and that CoMo-T2 would increase the conversion of coals with high proportions of ether linkages, or ethers within aromatic systems, and reduce formation of phenols from the reaction of these linkages. Liquefaction studies were performed on coals of differing rank and oxygen content. ATTM improved the conversion of all the coals. Product quality from Wyodak was also improved, by increasing oil yields without a significant increase in the proportion of phenols in the oil fraction. CoMo-T2 also improved conversion of all the coals. Improvement of product quality was achieved for Illinois #6 and the Pittsburgh #8, by increasing oil formation and reducing the phenolic fraction within the oils.

Chapter 9 deals with the effects of mineral matter in low-temperature liquefaction of low-rank coals. Depending on reaction conditions, the mineral and inorganic species present in coals can act as catalysts or poisons during liquefaction. For example, clays, the dominant mineral species in many coals, may be possible acid cracking catalysts and pyrite, the predominant sulfide form, is a well-documented hydrogenation catalyst; however cations, common in low rank coals, block access to pores or reaction sites. Several previous studies have observed a favorable influence of demineralization on coal depolymerization, specifically upon removal of naturally occurring cations such as Na^+ , Ca^{2+} and K^+ . The aim of this work was to evaluate the nature and distribution of mineral matter in both untreated and treated (demineralized) samples of Wyodak coal, and consider the influence of these compounds by assessing their possible catalytic effect. A series of experiments has been undertaken to compare the effect of demineralization on coal conversion at low temperatures (*ca* 300-350°C), where preliminary results indicated that conversions were comparable upon pretreatment.

The results show that relative to runs at 350°C with untreated coal, demineralization affords higher overall conversions; this increase in conversion is the result of increased gas make over soluble products. This trend becomes more apparent when either an H-donor (tetralin) or non-donor (1-MN) solvent are used. Specifically, there is no evident mineral matter effect on solvent H donation acting only in solvent capacity. Comparison of the two sets of data suggests that the reactions undergone at 350°C are not mineral matter catalyzed. Indeed, the main effect of the acid treatments reported here is to open the coal structure, thus promoting more intimate contact between the solvent and the coal interior.

Chapter 10 reports on a new development in our research on catalytic liquefaction. Here we report on the effect of water addition on in situ generated dispersed Mo catalysts for hydrogenation and C-O bond hydrogenolysis of 2,2'-dinaphthyl ether, abbreviated as DNE. In our recent work we found that the addition of water has a strong promoting effect on low-severity catalytic coal liquefaction using in-situ generated MoS₂ catalyst. In order to clarify the role of water, model reactions of 2,2'-dinaphthyl ether (DNE) were carried out using ammonium tetrathiomolybdate (ATTM) as catalyst precursor in the absence and presence of H₂O or D₂O. The addition of water to the non-catalytic runs of DNE has no effect at 350 - 400 °C, but the use of ATTM increased DNE conversion. Addition of H₂O significantly promoted DNE conversion and the yields of C-O bond cleavage products as well as their hydrogenation.

To clarify the effect of water on the catalytic activity, two-step reactions were carried out. Catalysts were prepared from the runs using ATTM with and without water, and then DNE was hydrogenated with and without water. After the preparation of catalyst from ATTM and water, the removal of water prior to the reaction causes complete conversion of DNE; on the other hand, after the preparation of catalyst from the run using ATTM alone, an addition of water decreases the conversion of DNE. These results suggest that addition of proper amount of water is effective for the in-situ generation of active Mo sulfide catalyst from ATTM for hydrogenation of DNE, but water itself does not have positive effect on DNE conversion.

It is very interesting to note that the model compound studies clearly established that there is a strong promoting effect of water on the catalytic runs at relatively low temperatures using dispersed ammonium tetrathiomolybdate as catalyst precursor.

Chapter 11 reports on boiling point analysis of heavy liquids by simulated distillation using gas chromatograph. This work was a part of our effort to establish a method for analyzing the liquids from coal/petroleum coprocessing and coal liquefaction. In order to facilitate the analytical work of both the starting materials and the upgrading products, we have used petroleum resids.

Two petroleum resids and their products from catalytic upgrading were characterized by high-temperature simulated distillation using gas chromatograph (HT-SimDis GC) with a capillary column. The range of atmospheric equivalent boiling point (AEBP) determined by the HT-SimDis GC method established in this work covered very high end of up to 847°C (1557°F). It has been successfully applied for analyzing the AEBP distribution of an atmospheric resid and a vacuum resid as well as their products from catalytic hydroprocessing. The analysis of the AEBP distribution versus reaction temperature revealed that catalytic upgrading can not only produce lighter fractions, but also create desirable changes in the remaining >540°C fractions. For the runs over a sulfided Co-Mo/Al₂O₃ catalyst, the yields of products with BP range of 540-700°C remained almost constant when the reaction temperature was within 350-400°C, but decreased monotonically with further increasing reaction temperature up to 450°C. At high temperature (450°C), 450-540°C fraction is also converted simultaneously. The extent of catalytic hydrodesulfurization over Co-Mo/Al₂O₃ catalyst increased with increase in temperature from 350 to 450°C.

Finally, included in the Appendix is a list of publications during 1992-1997 related to this project. There are some more results or more experimental details that were not included in this final report due to limited space and time, but in such cases most of them have been reported in preliminary forms in the previous technical progress reports TPR 1 through TPR-16. The publication list in the Appendix includes some papers that were not generated solely from this DOE project, but our thinking and concepts developed from this project were partly incorporated in those papers. Therefore, it is the support from DOE that led us to create new knowledge and information described in those papers listed in the Appendix section.

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Chapter 1

Synthetic Preparation of Organometallic Bimetallic Compounds as Catalyst Precursors Containing Mo and Co

Introduction

Direct coal liquefaction is the process for producing liquid fuel from coal and involves the reactions of coal with reducing gas (H_2) in a solvent vehicle at high temperature and high pressure. On the microscopic level, the coal conversion into liquids is an extremely complex process and involves both chemical and physical transformations. Despite enormous strides in coal liquefaction research, and great effort at Wilsonville Advanced Two-Stage Liquefaction Facility to reduce the cost of coal-derived distillates, coal-derived liquids are still not competitive with petroleum crudes. Further improvements are required and the most promising approach would be the development of improved catalytic process. It is known that direct coal liquefaction proceeds through two loosely defined stages, coal dissolution into solvent-soluble materials, followed by upgrading of the solubilized products. The distribution and quality of primary liquefaction (coal dissolution) products depend on the coal, catalyst, solvent and process conditions used in the first stage. The upgrading of primary liquefaction products into transportation fuels requires two conversion steps: an overall upgrading of heavy materials to distillate materials, followed by the upgrading of different distillate fractions to liquid products with the necessary properties for use as transportation fuels including gasoline, jet fuels, and diesel fuels.

Numerous studies have been conducted of the application or improvement of conventional catalysts and of the development of new catalysts for hydroliquefaction of coals. As indicated by Derbyshire (1988, 1990), research on catalytic liquefaction has been retarded by the persistent and misguided belief that catalysts cannot influence the reactions whereby the solid coal feed is converted to soluble products. It is relatively easy for conventional supported catalysts to promote the reactions after the primary liquids are formed. However, by this time the most critical reactions may have taken place and distributions of products may have already been determined (DOE COLIRN Panel, 1989). In this respect, dispersed catalysts are superior because they may be able to affect the coal dissolution due to their more intimate contact with coal. Monitoring the change of system pressure for catalytic reactions has clearly demonstrated that some dispersed Ni and Mo catalysts can promote the hydrogenation reactions of coals at fairly low temperatures, as revealed by the considerable H_2 uptake at 300-350 °C (Bockrath et al., 1990; Song et al., 1991a). Some novel Lewis acidic Ni and Mo catalysts also enhance the

coal pyrolysis at temperatures as low as 300°C, even under N₂ atmosphere (Song et al., 1986a, 1987a, 1991a).

Extensive research at Pittsburgh Energy Technology Center, PETC (Bockrath et al., 1984, 1986, 1991; Utz et al., 1989; Cugini et al., 1991a, 1991b) and Penn State (Davis et al., 1986, 1989; Derbyshire et al., 1986a, 1986b, 1989; Stansberry et al., 1987; Burgess and Schobert, 1990; Burgess et al., 1991; Artok et al., 1991) has demonstrated the potential of using dispersed molybdenum or iron catalyst. The work at Penn State has demonstrated that the combination of low-temperature catalytic reaction followed by the high temperature catalytic reaction using dispersed molybdenum significantly enhanced coal conversion and oil production. More recent work in this laboratory has shown that temperature-programmed liquefaction is more effective for converting low rank coals (Song et al., 1991b; Song and Schobert, 1992b; Huang et al., 1992). We have found that low-temperature catalytic reactions using dispersed Mo catalyst lead to some desirable changes in coal structure, and the temperature-programmed catalytic liquefaction affords considerably higher conversion than the conventional non-programmed or the temperature-staged liquefaction (Song et al., 1992b; Huang et al., 1992). All these results point to the beneficial effects of dispersed catalysts for lower-severity liquefaction, and clearly indicate that dispersed catalysts could significantly affect the chemistry of initial coal dissolution (primary liquefaction) and reduce undesirable reactions. It should be noted that almost all of the previous work used precursors of single transition metal sulfides, and little has been reported about bimetallic dispersed catalysts.

Development of new catalysts is a promising approach to more efficient coal liquefaction. Coal conversion catalysis is a comparatively immature field. Perhaps the most promising approach to the development of novel catalysts lies in research into multi-component systems, which, compared to the work with single metal catalysts, are essentially unexplored (Derbyshire, 1990). Several reports have demonstrated on the synergistic effects for multi-component Lewis acidic Zn-, Ni-, and Mo-based catalysts for coal liquefaction or model reactions (Mobley and Bell, 1980; Song et al., 1986a, 1988a, 1991a). Synergism has been reported for Fe-Mo catalysts by Garg and Givens (1984). Even under high-severity conditions (440°C, 2000 psi H₂), significant benefits were observed by using Fe and Mo together; simultaneous impregnation of coal with Fe and Mo significantly increased coal, preasphaltene and asphaltene conversion as compared to individual metals for liquefaction of a Kentucky bituminous coal in the presence of SRC-II heavy distillate. There are clear evidences of the synergism for two or multi-component supported catalysts in the field of heterogeneous catalysis, especially hydrotreating catalysts such as Co-Mo and Ni-Mo. We can anticipate that synergistic effects of multicomponent dispersed

catalysts could lead to significantly improved catalytic processes for direct conversion of coal to transportation fuels.

Emphasis for developing novel catalytic process should be directed at promoting the direct transformation of coal to distillates that have low aromaticity and low heteroatom content . This is primarily because the 1990 Clean Air Act Amendments and the increased worldwide concern about global warming will require the production of liquid transportation fuels from coals be based on new strategy away from the formation of aromatic products and more toward formation of hydrogen-rich aliphatic hydrocarbons. Equally important, novel catalysts should promote coal conversion into low-molecular-weight products and their hydrogenation at lower-severity conditions. The present research is a fundamental and exploratory study on catalytic coal liquefaction, with the emphasis placed on exploring novel bimetallic dispersed catalysts for temperature-programmed liquefaction.

The primary objective of this research is to explore novel bimetallic dispersed catalysts from organometallic molecular precursors, that can be used in low concentrations ($<1\%$) but exhibit high activity for efficient hydroliquefaction of coals under temperature-programmed conditions. The first technical approach is to prepare the desired heteronuclear organometallic molecules as catalyst precursors that contain covalently bound, two different metal atoms and sulfur in a single molecule. The second approach is to perform the liquefaction of coals impregnated with the organometallic precursors under temperature-programmed conditions, where the programmed heat-up serves as a step for both catalyst activation and coal pretreatment or preconversion. Concordant with the goal of developing an efficient catalytic liquefaction process, we seek to understand the functions of the new catalysts and their effects on product quality by performing the tests using model reactions of aromatic and polar compounds that are relevant to coal liquefaction.

Methodology for Synthetic Preparation of Catalyst Precursors

The initial effort of this project was focused on selecting and synthesizing the organometallic compounds that contain two different transition metals and sulfur in a single cluster. The first candidate was Co-Mo bimetallic complexes. In general, the synthesis was carried out using the published procedures, and the preferable procedures were selected based on the metal species of interest, simplicity, and ease to scale up in the future.

There are several types of complexes containing the same metal species (for example, Co-Mo). The first method to be used is the procedure for synthesis of thiocubane cluster, which was originally developed by Brunner and Watcher (1982). The reaction for preparing Mo-Co thiocubane, $(C_5H_5)_2Mo_2Co_2S_4(CO)_2$ (*II*), is shown in equation 1. Compound *II* can be prepared by adding *IB* to the brown solution of *IA* in toluene.

There are several other methods for synthesizing bimetallic complexes (Muller et al., 1971, Brunner et al., 1983; Halbert et al., 1985; Dias et al., 1985). Another general method is the procedure developed by Muller et al. (1971). Bimetallic transition metal thioanions with d^0 -configuration of the central atom form complexes with ions of first transition series. As shown in equation 2, MoS_4^{2-} ion (*IIIA*) forms complexes with transition metals (*IIIB*), which can be isolated in the form of the tetraphenylphosphonium salts (*IV*). The synthesis shown in equation 2 is simple and can be applied for preparing Fe-Mo, Co-Mo, Ni-Mo, and Zn-Mo bimetallic complexes. Bimetallic complexes of Ni-Mo and Zn-Mo are stable as the $[M(MoS_4)_2]^{2-}$ dianions. However, bimetallic complexes of Co-Mo and Fe-Mo are only stable as the $[M(MoS_4)_2]^{3-}$ trianions. They should be prepared according to equation 2B), whose details can be seen from Scheme VI.

Bimetallic Catalyst Precursors Prepared

Scheme I gives a list of the bimetallic compounds prepared. All the bimetallic compounds were synthesized under a N_2 atmosphere using reagent-grade chemicals of the highest purity. Three bimetallic thiocubanes were used as catalytic precursors: $Mo_2Co_2S_4(S_2CNEt_2)_2(CH_3CN)_2(CO)_2$ [designated as MoCo-TC1], $Mo_2Co_2S_4Cp_2(CO)_2$ [MoCo-TC2], and $Mo_2Co_2S_4(Cp')_2(CO)_2$ [MoCo-TC3], in which Et, Cp and Cp' represent ethyl, cyclopentadiene, and pentamethylcyclopentadiene, respectively. These thiocubanes were synthesized in our laboratory based on the procedures of Brunner and Watcher [1982] and Halbert et al. [1985]. For comparative examination, the trianionic bimetallic complex, $(PPh_4)_3Co(MoS_4)_2$, was also synthesized based on the procedure of Pan et al. [1985]. This bimetallic sulfide complex contains cobalt bis-tetrathiomolybdate trianion, $Co(MoS_4)_2^{3-}$, and is designated as MoCo-S.

The Synthesis of $Mo_2Co_2S_4(S_2CNEt_2)_2(CH_3CN)_2(CO)_2$, MoCo-TC1

All reactions were carried out in a N_2 atmosphere. Triphenylphosphine, $Co_2(CO)_8$ (Strem), sublimed sulfur, acetonitrile (Baker), $(NH_4)_2MoS_4$, dimethylformamide, tetraethylammonium bromide, diethyldithiocarbamic acid sodium salt trihydrate (Aldrich), and toluene, methylene chloride (Fisher) were used as purchased from the respective suppliers. Scheme II gives the procedure for synthesis of MoCo-TC1, and Scheme III shows its structure.

ATTM (3.022 g, 11.6 mmole), sulfur (3.018 g, 15.7 moles), and DMF (50 ml) were placed in a 250 ml three-neck flask equipped with a condenser, stirbar, thermometer, and a N_2 inlet and outlet. A heating mantle was used to heat the solution to $95^\circ C$. The solution was allowed to stir for 3.5 hours before NEt_4Br was added. After 40 minutes the volatile components were removed by rotary evaporation. The resulting solid was dissolved in acetonitrile and filtered through a Buchner funnel. The volatile components in the filtrate were removed by rotary evaporation to yield a brick-red solid, $[NEt_4]_2[Mo_2S_{12}]$ (7.23 mmole).

$[NEt_4]_2[Mo_2S_{12}]$ (7.23 mmole), diethyldithiocarbamic acid sodium salt trihydrate (4.8903, 21.7 mmole), triphenylphosphine (11.383 g, 23.1 mmole), NH_4PF_6 (7.072 g, 23.1 mmole), and acetonitrile (100 ml) were placed in a three-neck 250 ml round-bottom flask equipped with a stirbar, condenser, N_2 inlet and outlet and heated for 50 minutes at $75^\circ C$ before allowing the solution to cool to room temperature. The solution is dark orange-red while the

large amounts of white insoluble solids give the stirred solution a cloudy orange tinted brown color. The contents were transferred to a 250 ml flask and the volatile components were removed by rotary evaporation. The primary product, $\text{Mo}_2\text{S}_4(\text{S}_2\text{CNEt}_2)_2$, was purified by TLC by eluting with CH_3CN .

$\text{Mo}_2\text{S}_4(\text{S}_2\text{CNEt}_2)_2$ and $\text{Co}_2(\text{CO})_8$ (2.51 g, 7.34 mmol) were added to 30 ml CH_3CN in a three-neck 250 ml flask equipped with a stirbar, and a N_2 inlet and outlet. The solution was allowed to stir for five hours at room temperature before the solution was filtered. The acetonitrile-soluble portion had the solvent removed by rotary evaporation. The product was dissolved in methylene chloride before being applied onto the TLC plate; the eluting solvent, acetonitrile, gave an olive-green product. Yield of $\text{Mo}_2\text{Co}_2\text{S}_4(\text{S}_2\text{CNEt}_2)_2(\text{CH}_3\text{CN})_2(\text{CO})_2$, 1.430 g, 1.627 mmol, 14% (literature yield: 20%).

Synthesis of $\text{Mo}_2\text{Co}_2\text{S}_4\text{Cp}_2(\text{CO})_2$, MoCo-TC2

All reactions were carried out under a N_2 atmosphere. $\text{Mo}(\text{CO})_6$ and $\text{Co}_2(\text{CO})_8$ (Strem), dicyclopentadiene and n-decane (Aldrich), HPLC-grade toluene (Fisher), and sublimed sulfur (Baker) were used as purchased from the respective suppliers. Scheme IV gives the procedure for synthesis of MoCo-TC2, and Scheme V shows its structure.

$\text{Mo}(\text{CO})_6$ (4.038 g, 15.3 mmol), dicyclopentadiene (1.2 ml, 1.183 g, 8.95 mmol), and 50 ml n-decane were placed in a 250 ml three-neck round bottom flask equipped with a condenser, stirbar, N_2 inlet and outlet, and a thermometer. An oil bath was used to bring the solution to reflux ($\sim 175^\circ\text{C}$). The solution started out as colorless with $\text{Mo}(\text{CO})_6$ being only slightly soluble in the n-decane at room temperature, but as the temperature increased $\text{Mo}(\text{CO})_6$ became completely soluble. The solution started to turn yellowish at around 90°C and brownish at around 130°C ; sublimation of $\text{Mo}(\text{CO})_6$ as white crystals on the sides of the flask started around 110°C . It took around 45 minutes for refluxing to occur (by this time the solution was an opaque dark brown with a substantial amount of white gas throughout the flask). Reflux was allowed to continue for about five hours longer during which the white crystals of $\text{Mo}(\text{CO})_6$ were periodically washed with n-decane and scraped with a spatula from the sides of the flask throughout the reaction. The solution was filtered with n-decane into a 500 ml round bottom flask leaving a blackish residue and a very dark red filtrate. The residue was discarded and the filtrate had the volatile components removed by rotary evaporation to yield a brick-red solid, $\text{Mo}_2\text{Cp}_2(\text{CO})_4$ with some $\text{Mo}_2\text{Cp}_2(\text{CO})_6$ as a by-product.

The brick-red solid, $\text{Mo}_2\text{Cp}_2(\text{CO})_4$, was dissolved in toluene and filtered again giving a residue and a red filtrate. The red filtrate was placed in a 250 ml two-neck round bottom flask with Sg (0.555 g, 2.16 mmoles) and 50 ml toluene. The round bottom flask was equipped with a condenser, stirbar, and a N_2 inlet and outlet. The oil bath that heated the flask was monitored with a thermometer. The mixture was allowed to stir overnight (16-20 h) at 50°C whereby the solution was filtered with toluene into another flask giving a grayish-green residue and a brownish-red filtrate, $\text{Mo}_2\text{Cp}_2\text{S}_4$.

The brownish-red filtrate, $\text{Mo}_2\text{Cp}_2\text{S}_4$, was dried to a solid by rotary evaporation to find the mass and was subsequently placed in a 250 ml two-neck flask equipped with a stirbar and a N_2 inlet and outlet. Toluene (50 ml) was added and the dark brownish-red solution was stirred for ten minutes before $\text{Co}_2(\text{CO})_8$ (0.940g, 2.75 mmoles) was slowly added. Small bubbles formed almost immediately upon the introduction of $\text{Co}_2(\text{CO})_8$ due to the release of free CO from $\text{Co}_2(\text{CO})_8$. The reaction was allowed to stir for thirty minutes more whereby the solution was observed to have a increasingly purplish cast. The solution was filtered with toluene giving a dark residue and a violet filtrate. A dark violet solid was obtained after rotary evaporation of the filtrate.

The dark violet solid was dissolved in methylene chloride and applied to a thin-layer chromatography silica gel plate (Whatman PK6F, silica gel 20 cm x 20 cm plates, 1 mm thick, 60 Å particles). The eluting solvent was toluene. The only band to appear was a purple band with reddish-purple trailings which came off quite easily using only toluene. The purple band was extracted from the thin-layer chromatography plate with methylene chloride through a water-aspirated fritted filter giving a dark violet solution. The dark violet solution was transferred to a round bottom flask where the solvent was removed by rotary evaporation. The violet solid was vacuum dried at 45°C for two hours to remove any trace of solvent. The product, $\text{Mo}_2\text{Co}_2\text{S}_4\text{Cp}_2(\text{CO})_2$, was stored under a N_2 atmosphere in a vial and placed in the freezer. A typical yield of $\text{Mo}_2\text{Co}_2\text{S}_4\text{Cp}_2(\text{CO})_2$ is 16% based on molybdenum in $\text{Mo}(\text{CO})_6$ (literature yield 18%).

Observations

One observation is that the first step is very touchy; there was a large variation in the product even when the experimental procedure was followed closely. If the conditions aren't harsh enough a reaction to the desired product, $\text{Mo}_2\text{Cp}_2(\text{CO})_4$, doesn't occur and if the

conditions are too harsh the reactants decompose into molybdenum metal and organic polymeric sludge.

There is an equilibrium in the reaction of Mo(CO)_6 and dicyclopentadiene between the desired product, $\text{Mo}_2\text{Cp}_2(\text{CO})_4$, which has a highly reactive triple bond between the two molybdenum centers, and $\text{Mo}_2\text{Cp}_2(\text{CO})_6$, which has a single bond between the two molybdenum centers. The equilibrium favors $\text{Mo}_2\text{Cp}_2(\text{CO})_4$ at higher temperatures thus necessitating a high boiling point solvent such as decane (bp 175°C). $\text{Mo}_2\text{Cp}_2(\text{CO})_6$ would be the major product if the reaction was carried out in refluxing toluene (bp 110°C). Decane was found to be a better solvent for the reaction of Mo(CO)_6 and dicyclopentadiene than p-cymene (bp 175°C), possibly due to the greater polarity of p-cymene. Sometimes an insoluble polymeric sludge was formed during the first step when p-cymene was used.

During the reaction between $\text{Mo}_2\text{Cp}_2\text{S}_4$ and $\text{Co}_2(\text{CO})_8$, sometimes a small amount of $\text{Co}_2(\text{CO})_8$ (around 0.2 g, 0.4 mmoles) was added to the reaction mixture after thirty minutes to see if the reaction was complete. The reaction was determined complete if there weren't any bubbles observed when the extra $\text{Co}_2(\text{CO})_8$ was added to the solution.

Methylene chloride was determined to be a better solvent than toluene to dissolve the product in before being applied to the thin-layer chromatography silica gel plate and when the product was extracted from the silica gel. The product was always found to be "wet" when toluene was used; this could be due to the lower vapor pressure of toluene compared to that of methylene chloride at the relatively low temperatures ($40\text{--}50^\circ\text{C}$) during the vacuum-drying stage of the final product.

Synthesis of $\text{Mo}_2\text{Co}_2\text{S}_4\text{Cp}'_2(\text{CO})_2$, MoCo-TC3

The procedure is the same as for MoCo-TC2, except that Cp'_2 [$(\text{C}_5\text{Me}_5)_2$, pentamethylcyclopentadiene] is substituted for Cp_2 [$(\text{C}_5\text{H}_6)_2$, cyclopentadiene] in the first step. The structure of MoCo-TC3 is also shown in Scheme V.

Scheme I

Organometallic Catalyst Precursors

Code	Molecular Formula	Structure
MoCo-TC1:	$\text{Mo}_2\text{Co}_2\text{S}_4(\text{S}_2\text{CNEt}_2)_2(\text{CH}_3\text{CN})_2(\text{CO})_2$	Thiocubane ^a
MoCo-TC3:	$\text{Mo}_2\text{Co}_2\text{S}_4(\text{Cp}')_2(\text{CO})_2$	Thiocubane ^b
MoCo-TC2:	$\text{Mo}_2\text{Co}_2\text{S}_4\text{Cp}_2(\text{CO})_2$	Thiocubane
MoCo-S	$(\text{PPh}_4)_3\text{Co}(\text{MoS}_4)_2$	Sulfide complex ^c
$\text{Mo}(\text{CO})_6$	$\text{Mo}(\text{CO})_6$	Metal Carbonyl
$\text{Co}_2(\text{CO})_8$	$\text{Co}_2(\text{CO})_8$	Metal Carbonyl

a) T.R.Halbert; S.A. Cohen; E.I. Stieffel Organometallics, 1985, 4, 1689-1690.

b) H. Brunner; J.J. Watcher; J. Organomet. Chem., 1982, 240, C41-C44.

c) W. Pan; D.C. Johnson; S.T. McKenna et al. Inorg. Chimica Acta, 1985, 97, L17-19

Scheme II

SYNTHESIS OF BIMETALLIC THIOCUBANE COMPOUNDS

Scheme III

STRUCTURE OF THE BIMETALLIC THIOCUBANE
MoCo-TC1

Scheme IV

SYNTHESES OF BIMETALLIC THIOCUBANE
COMPOUNDS

Scheme V

STRUCTURE OF BIMETALLIC THIOCUBANES MoCo-TC2 and MoCo-TC3

MoCo-TC2, R = C₅H₅-
MoCo-TC3, R = C₅Me₅-

Scheme VI

SYNTHESES OF BIMETALLIC SULFIDES

1) Dianionic compounds, $[M(M'S_4)_2]^{2-}$
 ($M' = Mo, M = Ni$; $M' = W, M = Ni, Co, Fe$)

2) Trianionic compounds, $[M(MoS_4)_2]^{3-}$
 $M = Co, Fe$

Scheme VII
**STRUCTURE OF BIMETALLIC INORGANIC
SULFIDE**

Synthesis of $(PPh_4)_3[Co(MoS_4)_2]$, MoCo-S

$CoCl_2 \cdot 6H_2O$ (Strem), triethylamine, thiophenol, ammonium tetrathiomolybdenum, tetraphenylphosphonium bromide (Aldrich), and acetonitrile (Baker) were used as received from the various suppliers. All reactions were carried out under a N_2 atmosphere except for the filtrations. Scheme VI gives the procedure for synthesis of bimetallic sulfide complexes including MoCo-S, and Scheme VII shows its structure.

$CoCl_2 \cdot 6H_2O$ (1.190 g, 5.00 mmol) was placed in a flask with 10 ml acetonitrile. The red-purple compound turned a brilliant blue in the acetonitrile solution. In a second flask, triethylamine (1.307 g, 12.9 mmol) and thiophenol (1.395 g, 12.7 mmol) were mixed together and then added to the $CoCl_2$ /acetonitrile solution. The resulting solution immediately became an olive-green and was then added to a mixture of ammonium tetrathiomolybdenum (2.619 g, 10.06 mmol) and 100 ml acetonitrile and allowed to stir for thirty minutes. The solution was filtered leaving a black residue and a very dark olive filtrate. Tetraphenylphosphonium bromide (5.423 g, 12.9 mmol) was added to the filtrate and allowed to stir for thirty minutes. The resulting precipitate was collected by repeated filtrations to give a very dark olive solid that is air sensitive. Yield: 2.501 g, 38.1 % (literature yield: variable, up to 70 %).

Observationss

MoCo-S is very air sensitive and is known to decompose in an aerobic solution in fifteen minutes. It must be dissolved in one of the few solvents (see below) that it is soluble in and then filtered to remove any decomposed material before any liquefaction work is done with it.

It is soluble in chloroform and methylene chloride but not in any of the common organic solvents (toluene, THF, etc) that are used in dispersing catalyst onto coal before liquefaction.

The performance of these bimetallic compounds as precursors to in-situ generated Mo-Co sulfide catalysts will be reported in the next quarter.

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Chapter 2

Bimetallic Dispersed Catalysts from Thiocubane Clusters for Temperature-Programmed Liquefaction

Introduction

Development of novel catalysts is a promising approach to more efficient coal liquefaction for producing clean transportation fuels including gasoline, diesel, and jet fuels. Jet fuels derived from coals are rich in cycloalkanes, and are not only alternative to, but also superior to, petroleum-derived jet fuels in terms of high thermal stability and high volumetric energy density.^{1,2} For primary coal liquefaction, it has been recognized that dispersed catalysts are superior to supported catalysts. The advantage of dispersed catalysts is largely due to their intimate contact with the surface of coal particles, which facilitates the activation and transfer of hydrogen to the coal-derived fragments and reactive sites. In general, increasing dispersion of active metals increases the catalyst's effectiveness. Because most active catalysts of interest (e.g., MoS₂) are insoluble in common solvents, the desire to achieve better dispersion leads to the strategy of using a soluble precursor that can be dispersed onto coal surface from its solution. The precursor may not be active itself, but it is transformed at elevated temperatures into an active catalyst.

Many reports have been published on liquefaction using dispersed metal sulfide catalysts, mostly molybdenum and iron sulfide, from a water-soluble inorganic salt or oil-soluble metal naphthenates.³⁻⁵ Organometallic compounds such as metal carbonyls have also been tested as catalyst precursors,⁶⁻⁹ which often require the addition of sulfur compounds, unless used with high-sulfur coals.⁶ The present work is concerned with heteronuclear organometallic precursors which can directly produce metal sulfides upon thermal decomposition. There are some unique advantages of organometallic compounds as catalyst precursors. First, most organometallic compounds are soluble in hydrocarbon solvents and may be used as oil-soluble precursors. Second, organometallic compounds can be easily decomposed to metal sulfides or oxides at low temperatures. This means they could form activated catalysts at lower temperatures, and this is apparently an advantage when compared to inorganic salt precursors which decompose at relatively higher temperatures.^{10,11} It is believed that the high activity coupled with high dispersion can allow catalyst concentrations of substantially less than 1 wt% to be used.

Little work on bimetallic dispersed sulfides for coal liquefaction has appeared.¹⁰ The advantage of using two metals in a single catalyst, however, has been demonstrated in the field of heterogeneous catalysis. It is well known that the addition of a second transition metal such as Co or Ni to MoS₂ or WS₂ can give rise to a significant increase in hydrogenation and hydrodesulfurization (HDS) activity.¹² Five-fold to ten-fold increases of HDS activity of the unpromoted sulfide upon addition of second transition metal sulfide are not uncommon for hydrotreating catalysts.¹³ Recently, Chianelli et al.¹⁴ have used the unsupported sulfides from bimetallic complexes to study the promotional effects of Co or Ni for MoS₂. However, in coal liquefaction the two-component dispersed metal sulfide catalysts are essentially unexplored.¹⁰ Previous work on multicomponent catalysts has involved mainly the mixture of two or more inorganic salts.¹⁵⁻¹⁹

Related to this work are the following two important and general observations from previous investigations. First, there could be synergistic effects between two different metal compounds;^{15,16,18} second, an organometallic precursor may be better than an inorganic one.^{10,11} Our interest in the heteronuclear organometallic compounds was stimulated by the recent book on metal clusters by Mingos and Wales.²⁰ Although this book contains no information on heterogeneous catalysis, it seemed to us that highly active catalysts might be prepared from some clusters containing metal-metal bonds, especially the "thiocubane" clusters containing two different metals and sulfur in a single molecule.

The primary objectives of the present work are to explore novel bimetallic dispersed catalysts from organometallic molecular precursors, that can be used in low concentrations (≤ 1 wt% metal) but exhibit high activity, and to optimize the performance of the best precursors for coal liquefaction by improving the reaction conditions and catalyst dispersion. Our first approach is to synthesize the heteronuclear complexes that contain two kinds of transition metals, Mo and Co, and sulfur in a single molecule. Two different metals bound together in a single compound should have a more systematic spatial arrangement in the resulting catalytic phase than if two separate compounds were used to introduce the two different metals to a catalytic system. Such bimetallic molecular precursors are expected to generate finely dispersed Mo-Co bimetallic sulfide catalysts upon thermal decomposition. The second approach is to perform the liquefaction of coals impregnated with the precursors under non-programmed and temperature-programmed (TPL) conditions, where the programmed heat-up serves as a step for both catalyst activation and coal pretreatment or preconversion. An increase in oil yields and coal conversions under temperature-programmed conditions has been observed in previous liquefaction studies with and without catalysts.^{21,22} In a preliminary communication, we

reported that a Mo-Co thiocubane is a promising catalyst precursor.²³ The third approach is to maximize the catalyst performance by improving the catalyst dispersion method.

This chapter describes our results on: 1) the effect of structure of the bimetallic precursors on their catalytic activity for liquefaction of a Montana subbituminous coal; 2) the effect of temperature programming on catalytic and thermal liquefaction in non-donor and hydrogen-donor vehicles; 3) influence of the catalyst dispersion method; and 4) the catalytic effects of mixed metal carbonyls, $\text{Mo(CO)}_6 + \text{Co}_2(\text{CO})_8$, and the comparison between the bimetallic thiocubane molecular precursor and the corresponding mixtures of metal carbonyls and the mixed metal carbonyls plus added sulfur.

Experimental Procedures

Catalyst Precursors and Coal Samples

All the bimetallic compounds were synthesized under a N_2 atmosphere using reagent-grade chemicals of the highest purity. Three bimetallic thiocubanes were used as catalytic precursors: $\text{Mo}_2\text{Co}_2\text{S}_4(\text{S}_2\text{CNEt}_2)_2(\text{CH}_3\text{CN})_2(\text{CO})_2$ [designated as MoCo-TC1], $\text{Mo}_2\text{Co}_2\text{S}_4\text{Cp}_2(\text{CO})_2$ [MoCo-TC2], and $\text{Mo}_2\text{Co}_2\text{S}_4(\text{Cp}')_2(\text{CO})_2$ [MoCo-TC3], in which Et, Cp and Cp' represent ethyl, cyclopentadiene, and pentamethylcyclopentadiene, respectively. These thiocubanes were synthesized in our laboratory based on the procedures of Brunner and Watcher²⁴ and Halbert et al.²⁵ For comparative examination, the trianionic bimetallic complex, $(\text{PPh}_4)_3\text{Co}(\text{MoS}_4)_2$, was also synthesized based on the procedure of Pan et al.²⁶ This bimetallic sulfide complex contains cobalt bis-tetrathiomolybdate trianion, $\text{Co}(\text{MoS}_4)_2^{3-}$, and is designated as MoCo-S.

The coal sample used was a Montana subbituminous coal, which is one of the U.S. Department of Energy Coal Samples (DECS-9) obtained from the Penn State/DOE Coal Sample Bank. The DECS-9 (PSOC-1646) coal (< 60 mesh) was stored under argon atmosphere in heat-sealed foil bags and has the following composition: 24.7% moisture, 4.8% ash, 33.5% volatile matter, and 37.1% fixed carbon on an as-received basis; 76.1% carbon, 5.1% hydrogen, 0.9% nitrogen, 0.3% organic sulfur, and 17.5% oxygen on a dmmf basis. The coal was dried in a vacuum oven at 100°C before use.

Some tests were conducted using the Pittsburgh #8 bituminous coal (DECS-12, PSOC-1549, < 60 mesh). DECS-12 sample has the following composition: 2.4% moisture, 10.0% ash,

35.2% volatile matter, and 52.4% fixed carbon on an as-received basis; 84.8% carbon, 5.7% hydrogen, 1.4% nitrogen, 0.7% organic sulfur, and 6.5% oxygen on a dmmf basis. The coal was dried for two hours at 100°C in a vacuum oven before use.

Incipient Wetness Impregnation of Catalyst

The catalytic precursors were dispersed onto the coal by the incipient wetness impregnation (IWI) method using organic solvents. Because of the difference in the solubility of the organometallic precursors, several organic solvents including toluene, tetrahydrofuran (THF), CHCl_3 , CH_2Cl_2 and acetonitrile were used for dissolving them. The organic solution of a precursor was intermittently added dropwise to the dried coal in a 100 mL beaker, in such a fashion that the wet spots over the coal particles do not touch each other, followed by manual stirring with a glass rod until all signs of wetness disappeared. In order to keep the metal loading from different precursors at a constant level, we first estimated the incipient wetness volume prior to the catalyst impregnation with a given solvent, which means the total volume of the solvent needed to reach the point of incipient wetness: the point when the solution drops begin to remain on the external surface of the coal. The loading for the bimetallic thiocubanes was 0.5 wt% of molybdenum on the basis of dmmf coal. The impregnated coal sample was dried at 100°C for 2 h in a vacuum oven. IWI method was applied to coal liquefaction in a previous work using aqueous solution.²² For catalyst preparation, IWI method is often used for loading inorganic salts from their aqueous solution onto a porous support.²⁷ It should be noted that the IWI method used in our work is different from the conventional one in that we only use a certain amount of solution defined by the estimated incipient wetness volume to achieve a constant metal loading.

Swelling Impregnation with a Binary Solvent

In the experiments for testing the effect of catalyst dispersion methods, some catalyst precursors were dissolved into a equal-volume mixture of toluene and THF. Excess amount of solvent, usually 5 mL binary solvent per g coal, was used. The predried coal powders were added to this solvent, and the slurry was stirred at 60 °C for about 20 h under a nitrogen atmosphere. The solvent was then removed by rotary evaporation, and the catalyst-impregnated coal samples were further dried in a vacuum oven at 100 °C for 2 h before use. THF is a known good swelling solvent for coal but toluene has very limited, if any, swelling ability. The reason we chose such a binary mixture as a swelling solvent is because some bimetallic precursors can not be dissolved in THF alone but can be soluble in the mixture of toluene-THF. An additional reason is that for the IWI method, using toluene solvent to impregnate MoCo-TC2 gave better or similar results relative to the use of THF solvent alone. The loading for the bimetallic

thiocubanes was 0.5 wt % Mo on dmmf coal. When Mo(CO)_6 and $\text{Co}_2(\text{CO})_8$ were used, the loading was 0.5 wt % for Mo and 0.3 wt % for Co based on dmmf coal.

Liquefaction under SSL and TPL Conditions

All reactions were carried out in 25 mL tubing bomb microautoclaves in a temperature-controlled fluidized sandbath. Each reaction used approximately 3 g dried coal. 1-Methylnaphthalene was used as the reaction solvent (3 g) unless otherwise mentioned. In several experiments tetralin was also used as a hydrogen-donor solvent (3 g) for comparison. The initial H_2 pressure was 7 MPa at room temperature for all the runs. A fluidized sand bath was used as the heater, where the agitation of the reactants in the reactor is achieved via an oscillator by vertical shaking of the horizontal tubing bomb (about 60 strokes per minute).

For catalyst screening, single-stage liquefaction (SSL) was performed, where the tubing bomb was rapidly heated to the prescribed temperatures (400–425 °C) for 30 minutes (plus a three minute heat-up period) followed by a rapid quench in cold water bath. Temperature-programmed liquefaction (TPL) had the tubing bomb rapidly heated up to a low temperature (200 °C) and soaked at that temperature for 15 minutes before the temperature was gradually increased (5–7°C/min) to a higher temperature (400°C–425°C) and held there for 30 minutes before rapid quenching with cold water bath. The TPL procedures were developed in our recent work.^{21,22}

The gaseous product was vented after the reaction was complete and the liquid and solid products were washed into a ceramic thimble with hexane. The products were separated under a N_2 atmosphere by Soxhlet-extraction using hexane, toluene, and THF in succession. Solvents were removed by rotary evaporation under reduced pressure. The hexane-soluble products are defined as the oil fraction. The asphaltene (toluene soluble, but hexane insoluble) and preasphaltene (THF soluble, but toluene insoluble) products were dried in vacuum at 100°C for 6 h before weighing. The THF-insoluble residues were washed with acetone and pentane and subsequently dried at 100 °C for over 6 h before weighing. The conversion was calculated based on dmmf coal as follows:

Conversion (dmmf wt %)

$$= [(\text{wt of dmmf coal} - \text{wt of dmmf residue}) / \text{wt of dmmf coal}] \times 100 \%$$

All the runs were repeated at least once or twice to confirm the reproducibility. In most cases, the experimental errors were within ± 2 wt% for total conversion, and the average data from two or more repeated runs are reported here.

Results and Discussion

Figure 2.1 shows the structures of the thiocubanes. The basic difference between these three thiocubanes is the type of ligands bound to the Mo [$\text{Cp} = \text{C}_5\text{H}_5$, $\text{Cp}' = \text{C}_5\text{Me}_5$; all the five carbon atoms in the cyclopentadiene ring are equidistant from the metal atom]. Figure 2.2 shows the structure of the $\text{Co}(\text{MoS}_4)_2^{3-}$ trianion.

Effects of Precursor Type and IWI Solvents

Table 2.1 shows the results of catalyst screening for liquefaction of the Montana subbituminous coal at 400 °C for 30 min. We first prepared and tested $\text{Mo}_2\text{Co}_2\text{S}_4(\text{S}_2\text{CNEt}_2)_2(\text{CH}_3\text{CN})_2(\text{CO})_2$ [MoCo-TC1], which was first synthesized and used recently by Halbert et al.²⁸ in preparing a CoMo hydrotreating catalyst. Using MoCo-TC1 impregnated onto DECS-9 coal from acetonitrile, however, showed little catalytic effect for increasing conversion. Replacing CH_3CN with THF for impregnating MoCo-TC1 increased coal conversion relative to the thermal run by 14 wt%, but did not improve oil formation to any significant extent. In fact, we also performed tests using metal carbonyls, as also shown in Table 2.1. Clearly, the bimetallic precursor MoCo-TC1 is even less active than the simple carbonyl compound of either Mo or Co. It seems that the acetonitrile solution and the dithiocarbamate and acetonitrile ligands in MoCo-TC1 can poison the resulting catalyst under the conditions employed. This observation prompted us to prepare the thiocubane which contains no nitrogen in the ligands, leading to the synthesis of $\text{Mo}_2\text{Co}_2\text{S}_4\text{Cp}_2(\text{CO})_2$ [MoCo-TC2], and $\text{Mo}_2\text{Co}_2\text{S}_4(\text{Cp}')_2(\text{CO})_2$ [MoCo-TC3].

MoCo-TC2 impregnated from toluene afforded substantially higher conversion and oil yield; it is apparently much more active than MoCo-TC1. In fact, as shown in Figure 2.3, the pressure of the reactor system containing DECS-9 coal impregnated with MoCo-TC2 (from its toluene solution) began to drop after the initial heat-up, indicating the occurrence of uptake of gas-phase H_2 . This pressure-drop is due to the adsorption and dissociation of H_2 gas by the catalyst and subsequent hydrogen transfer to the coal species, as also observed for other dispersed catalyst systems.¹⁸ Table 2.2 presents the results of catalytic runs of DECS-9 coal at 425°C. MoCo-TC3 exhibited lower catalytic activity compared to MoCo-TC2. The coal

conversions with MoCo-TC3 were lower than those with MoCo-TC2 at both 400 and 425 °C. The structure and ligands of MoCo-TC3 and MoCo-TC2 are of the same nature, except that cyclopentadiene in MoCo-TC2 is substituted by pentamethylcyclopentadiene in MoCo-TC3.

In addition to toluene solvent (Tables 2.1 and 2.2), we also tested THF for the IWI of MoCo-TC2 which is soluble in both solvents. THF is a much better swelling solvent than toluene.²⁹ It was expected that MoCo-TC2 would afford greater conversion when THF was used as the impregnating solvent, since THF could penetrate the coal structure, which might improve the dispersion of the resulting Co-Mo bimetallic sulfide catalyst. Surprisingly, the catalytic liquefaction using MoCo-TC2 gave both higher oil yields and total conversion when toluene was used rather than THF, as can be seen from Tables 2.1 and 2.2. These results suggest that there is no apparent advantage of using THF as compared to toluene for loading MoCo-TC2 for the incipient wetness impregnation. However, THF is better than acetonitrile for impregnating MoCo-TC1, in terms of higher conversion (Table 2.1). MoCo-TC1 is insoluble in toluene. These results demonstrate that solvents used for loading the precursors by the IWI method are also influential, although the impregnating solvent was removed by vacuum drying before the liquefaction reaction.

As shown in Table 2.2, using MoCo-TC1 at 425 °C only slightly increased oil yield, but the total coal conversion with this precursor is even lower than the thermal run. This again points to the negative impact of the CH₃CN and S₂CNEt₂ ligands in MoCo-TC1 upon the resulting catalyst in coal liquefaction. Under comparable conditions the catalyst from MoCo-TC1 is much less active than that from MoCo-TC2, although an active catalyst could possibly be generated from the MoCo-TC1 precursor if it was first decomposed at a low temperature followed by venting and purging to remove those compounds that are catalyst poisons, and subsequently re-charged with H₂ gas and heated up. Therefore, a better catalyst could be generated in-situ from the bimetallic precursor without nitrogen-containing ligands. In fact, the best MoCo bimetallic sulfide catalyst is generated in-situ from MoCo-TC2 during liquefaction. The order of catalytic activity of the bimetallic catalysts at 425°C is the same as that observed from runs at 400°C: MoCo-TC2 > MoCo-TC3 >> MoCo-TC1.

In an attempt to examine the role of bonding between Co and Mo, we further prepared and tested the heterometallic compound (MoCo-S), (PPh₄)₃Co(MoS₄)₂, which has a distinctly different structure than the above-mentioned thiocubanes. Preliminary results in Table 2.1 and Table 2.2 reveal that MoCo-S is more active than MoCo-TC1 at both 400 and 425 °C but is much less active compared to MoCo-TC2. It was found that MoCo-S is air-sensitive which does

cause some technical problems. We further performed several tests using MoCo-S that was purified immediately before it was loaded onto the dried DECS-9 coal. This purification significantly improved the activity of resulting catalyst, as shown in Table 2.1. MoCo-S is more active than MoCo-TC1 and comparable (after purification) to MoCo-TC3. However, the fact that MoCo-S decomposes even during storage under a N₂ atmosphere in a refrigerator presents a practical problem.

Table 2.3 shows the effect of using the catalytic precursors on liquefaction of DECS-12 Pittsburgh #8 bituminous coal. At 400°C, the catalytic effects appear to be enhanced coal conversion to preasphaltene and asphaltene, with little increase in oil production relative to thermal run. At 425°C, using MoCo-TC2 increased total conversion significantly compared to the thermal run; it also promoted oil production moderately. However, increasing temperature from 400°C to 425°C caused decrease in total conversion both in thermal run and catalytic runs. In both cases, MoCo-TC2 was much more active than MoCo-TC1, although the latter was used under better conditions (TPL) than the former (SSL), as we further describe below. This again points to the negative impact of the CH₃CN and S₂CNEt₂ ligands in MoCo-TC1 upon the resulting catalyst in coal liquefaction. Therefore, it appears that an active MoCo bimetallic sulfide catalyst is generated in-situ from MoCo-TC2 during liquefaction. Under comparable conditions the catalyst from MoCo-TC1 is much less active, although an active catalyst could be generated also from this precursor if first decomposed at low temperature followed by venting and purging to remove poisonous compounds and followed by re-charging H₂ gas and heat-up.

From the data in Tables 2.1-2.3, MoCo-TC2 is apparently the best precursor and MoCo-TC1 is the worst precursor among the three thiocubanes which differ from each other only in the type of ligands bound to Mo. The bimetallic sulfide complex, MoCo-S, also produces a catalyst whose activity is lower than that from MoCo-TC3 at 400°C and close to MoCo-TC3 at 425°C. Overall, the performance of the bimetallic catalysts generated in-situ from the molecular and mixed precursors seems to follow the following order: MoCo-TC2 > MoCo-TC3 ≥ MoCo-S >> MoCo-TC1. Since the thiocubanes have identical core structure Co₂Mo₂S₄, the differences in catalytic activity between the three thiocubanes clearly indicate the importance of ligand type (Figure 2.1). In particular, nitrogen-containing ligands appear to be harmful to in-situ catalyst generation. In MoCo-TC2 or TC3, there are direct metal-metal bonds between Co-Mo, Co-Co, and Mo-Mo in addition to the sulfur-bridges (Figure 2.1), while in MoCo-S, the Co and Mo are bound through sulfur-bridge bonding but there are no direct metal-metal bonds (Figure 2.2). The superiority of MoCo-TC2 over MoCo-S, in terms of catalytic property and air-sensitivity, may suggest the importance of direct metal-metal bonding. However, besides the above-mentioned

difference in the structure, MoCo-S precursor also contains phosphorus. It is not clear at the present stage whether the tetraphenyl phosphonium cation affects the activity of bimetallic sulfide generated in-situ from the MoCo-S. The above results reveal that the structure of the precursor molecules can significantly affect the activity of the resulting bimetallic MoCo sulfide catalyst.

Effects of Temperature-Programming

The second task in this study is to optimize the performance of promising catalysts selected from the screening tests described above. As a means to increase conversion, the liquefaction of coals impregnated with the precursors was carried out under temperature-programmed (TPL) conditions, where the programmed heat-up could serve as a step for both catalyst activation (precursor decomposition to active phase) and coal pretreatment or preconversion.

Table 2.4 shows the effects of temperature-programming on both the catalytic and thermal runs of DECS-9 coal. The TPL conditions consist of a rapid heat-up from room temperature to 200 °C, soaking at 200 °C for 15 min, programmed heat-up from 200 to 400 °C at about 5 °C/min, followed by a 30 min holding period. In the presence of either MoCo-TC2 or MoCo-TC3, TPL runs in 1-MN always give higher conversions and higher oil yields than the corresponding SSL runs. At a final reaction temperature of 425°C with 1-MN solvent, TPL runs of DECS-9 coal using MoCo-TC2 or TC3 gave 13-15 wt% higher conversions and 5-10 wt% higher oil yields than the corresponding SSL runs. In distinct contrast to these results, TPL runs using the metal carbonyls, both Mo(CO)_6 and $\text{Co}_2(\text{CO})_8$, gave similar results to those from SSL runs.

Table 2.5 shows the effects of temperature-programming on the catalytic and thermal runs of DECS-12 bituminous coal. In the presence of either MoCo-TC2, TPL runs in 1-MN always give higher conversions and higher oil yields than the corresponding SSL runs. At a final reaction temperature of 425°C with 1-MN solvent, TPL runs of DECS-12 coal using MoCo-TC2 gave 13-15 wt% higher conversions and 5-11 wt% higher oil yields than the corresponding SSL runs. In general, the runs of DECS-12 bituminous coal often give higher yields of asphaltene+preasphaltene than those from DECS-9 subbituminous coal.

Figure 2.1 Structures of three MoCo bimetallic thiocubane clusters [MoCo-TC1: $Mo_2Co_2S_4(S_2CNEt_2)_2(CH_3CN)_2(CO)_2$; MoCo-TC2: $Mo_2Co_2S_4Cp_2(CO)_2$; MoCo-TC3: $Mo_2Co_2S_4(Cp')_2(CO)_2$]. Cp = cyclopentadiene; Cp' = pentamethylcyclopentadiene.

Figure 2.2 Effect of thiocubane precursor MoCo-TC2 impregnated onto DECS-9 coal (IWI with toluene) on reactor pressure at 400 °C with 1-MN solvent under 6.9 MPa (1000 psi) H₂ (cold).

Figure 2.3 Structure of the bimetallic sulfide complex $\text{Co}(\text{MoS}_4)_2^{3-}$
[cobalt bis(tetrathiomolybdate) trianion].

Table 2.1 Liquefaction of DECS-9 Coal over Dispersed Catalysts at 400 °C for 30 min

Catalyst precursor	Solvent for catalyst loading ^a	Reaction type	Conversion dmmf wt%	Products (wt%, dmmf)		
				Preasphalt.	Asphaltene	Oil ^b
None	None	SSL	32.2	6.8	9.4	16.0
MoCo-TC1	CH ₃ CN	SSL	32.8	5.2	4.8	22.8
MoCo-TC1	THF	SSL	46.3	14.8	12.8	18.7
MoCo-TC2	Toluene	SSL	74.6	24.2	18.0	32.4
MoCo-TC2	THF	SSL	67.4	23.7	17.9	25.8
MoCo-TC3	Toluene	TPL	71.5	19.9	17.8	33.8
Mo(CO) ₆	1-MN	SSL	52.3	16.5	10.6	25.2
Co ₂ (CO) ₈	1-MN	SSL	51.3	15.0	12.6	23.7
Mo(CO) ₆ + Co ₂ (CO) ₈	1-MN	SSL	60.6	17.8	18.9	23.9
MoCo-S ^c	CHCl ₃	SSL	49.8	16.0	12.6	21.3
MoCo-S ^d	CH ₂ Cl ₂	SSL	68.3	27.1	16.0	25.2

a) The impregnating solvent (for IWI) was removed by evaporation in vacuum before the reaction solvent 1-MN was added. b) Including yields of C₁-C₄ hydrocarbon gases, which are normally lower than 2 dmmf wt% at 400 °C, and those of CO and CO₂ gases. c) Used shortly after synthesis without further purification. Decomposition during storage was noticed. d) Used after further purification immediately before use. The purified MoCo-S was impregnated on to coal using excess amount of CH₂Cl₂ solution.

Table 2.2 Liquefaction of DECS-9 Montana Subbituminous Coal at 425°C for 30 min

Catalyst precursor	Solvent for catalyst loading ^a	Reaction Cond.	Conversion	Products (wt%, dmmf)		
			dmmf wt%	Preasphalt.	Asphaltene	Oil ^b
None	None	SSL	46.9	13.8	16.4	16.7
MoCo-TC1	THF	SSL	35.9	5.7	9.9	20.3
MoCo-TC2	Toluene	SSL	68.5	12.5	13.9	42.1
MoCo-TC2	THF	SSL	70.0	18.0	15.5	36.5
MoCo-TC3	Toluene	SSL	61.4	13.2	11.9	36.7
MoCo-S	CHCl ₃	SSL	59.2	13.2	11.1	34.9

a) Incipient wetness impregnation. b) Including gases.

Table 2.3 Liquefaction of Pittsburgh #8 Bituminous Coal in 1-MN at 400-425°C

Catalyst precursor	Solvent for catalyst impregn	Reaction temp °C	Reaction condition	Oil+ Gas dmmf wt%	Asphalt. dmmf wt%	Preasph. dmmf wt%	Tot Conv dmmf wt%
None	None	400	SSL	13.7	20.4	26.8	60.9
MoCo-TC1	THF	400	TPL	9.8	21.9	34.0	65.7
MoCo-TC2	Toluene	400	SSL	14.5	27.8	34.3	76.6
None	None	425	SSL	16.2	19.1	16.1	51.4
MoCo-TC1	THF	425	TPL	16.9	24.6	19.4	60.8
MoCo-TC2	Toluene	425	SSL	21.8	27.7	23.8	73.3

We need to answer the question as to why programmed heat-up (TPL) with bimetallic thiocubanes is better than rapid heat-up. The superiority of TPL over SSL in catalytic runs using MoCo-TC2 or MoCo-TC3 with 1-MN solvent could be due to: 1) more products from coal after longer residence time irrespective of catalyst, since a programmed heat-up (longer time) is included in TPL but SSL only involves a very rapid heat-up in about three minutes followed by reaction at 400 or 425°C; 2) reactions including precursor decomposition and catalytic reactions during programmed heat-up. The first is not the case, as demonstrated by the following facts. Both in the non-catalytic runs and in the catalytic runs using metal carbonyls (either $\text{Mo}(\text{CO})_6$ or $\text{Co}_2(\text{CO})_8$) with 1-MN solvent, using temperature programmed heat-up had little or no impact on the liquefaction of DECS-9 subbituminous coal, neither on total conversion nor on product distribution, as can be seen from Table 2.4. The desirable effects of TPL in 1-MN solvent, therefore, are associated with low-temperature reactions including decomposition of the bimetallic precursors to generate active catalysts and catalytic reactions during programmed heat-up. Since the thiocubane precursor MoCo-TC2 may not be very active by itself, its decomposition at low temperature, which could serve as an in-situ activation/generation of the active catalyst, may contribute to more effective hydrogenation of reactive fragments and aromatics at high temperature.

It is interesting to note from Table 2.4 that under TPL conditions using 1-MN solvent, increasing final temperature of all the catalytic runs from 400 to 425°C further increased coal conversions and oil yields considerably. In distinct contrast, under SSL conditions, increasing temperature of the catalytic runs (using MoCo-TC2, TC3) from 400 to 425°C caused marked decrease in the total conversions, which is a remarkable sign of significant retrogressive reactions. As pointed out in Song et al.,³⁰ the rate of coal thermal fragmentation is influenced by temperature and heating rate; very fast heating to high temperature would lead to extremely rapid fragmentation of coals, especially low-rank coals, that may exceed the capacity or rate of hydrogenation (H-donation) of the system, leading to significant retrogressive crosslinking. It is also likely that under SSL conditions (heating rates, $\geq 100^\circ\text{C}/\text{min}$) very fast radical formation begins to occur before transformation of MoCo-TC2 into an active phase is completed, resulting in an unbalance between the rate of radical formation and the rate of radical-capping by H from the catalyst surface, especially at a higher temperature. In TPL runs, however, the catalyst precursor decomposes to form an active bimetallic sulfide and the weak linkages are broken and stabilized during programmed heat-up, so that by the time the radical formation becomes considerable at high temperature (400-425°C), the catalyst is already activated and can provide dissociated hydrogen atoms to cap the thermally generated radicals. These mechanistic

considerations account for why using MoCo-TC2 or TC3 affords further increased conversion and oil yields under TPL conditions but gives decreased conversion under SSL conditions when the final reaction temperature is increased from 400 to 425 °C.

In regards to the catalytic effects associated with the reaction solvent, we compared the runs using the hydrogen-donor tetralin with those using the non-donor 1-MN solvent, as also shown in Table 2.4. The increases in conversion and oil yield due to catalyst are much higher when using a non-donor 1-MN solvent as compared to the runs using a H-donor tetralin (Table 2.3). For example, for SSL runs of DECS-9 coal at 400°C, using MoCo-TC2 increased coal conversion from about 32 to 75 wt% $[(75-32)/32 = 134\% \text{ increase}]$ with 1-MN, and from about 71 to 88 wt% [24% increase] with tetralin. In the presence of a H-donor solvent, the catalytic effects relative to thermal runs appear to be higher in SSL runs than under TPL conditions, as can be seen by comparing the thermal and catalytic runs with tetralin in Table 2.4.

The larger difference between catalytic TPL and SSL for MoCo-TC2 or MoCo-TC3 in a non-donor 1-MN solvent at 425°C also points to the importance of low-temperature hydrogen-transfer during heat-up, which can be aided by either catalysts dissociating molecular H₂ to hydrogen atoms or H-donor solvents donating hydrogen. In this context, for non-catalytic runs, the superiority of TPL over SSL in H-donor tetralin can be attributed to the H-transfer from the donor to the reactive fragments thermally generated from coal. In other words, the radical generation from DECS-9 upon rapid heat-up to high temperature in SSL may be exceeding the hydrogen-donating capacity of tetralin. The similarity between the coal conversion in TPL and SSL runs using MoCo-TC2 together with tetralin for DECS-9 indicates that using a good catalyst together with a good H-donor solvent can greatly enhance the radical-capping ability of the system, so that the role of low-temperature hydrogen-transfer reactions become less important for converting DECS-9 coal.

Effect of Catalyst Dispersion Methods

In the aforementioned experiments, all the bimetallic thiocubanes were loaded onto coal by the IWI method. It is also necessary to examine the effect of methods for catalyst loading which affect catalyst dispersion. As Weller³ pointed out ten years ago, the degree of dispersion is very important for the performance of unsupported catalysts in coal liquefaction. In the present study we examined four different methods for dispersing MoCo-TC2 in TPL.

Figure 2.4 shows that even the physical mixing of MoCo-TC2 with coal strongly enhanced coal conversion under TPL conditions. This result, however, must be interpreted with caution, because MoCo-TC2 is soluble in 1-MN, which is the reaction solvent. In the second method, we first dissolved MoCo-TC2 in 1-MN, and then added coal to the solution; this mixture was directly subjected to reaction. Figure 2.4 indicates that the latter method gave slightly higher conversion. It is clear from Figure 2.4 that using a solution of MoCo-TC2 in 1-MN for a catalytic reaction affords similar results to the MoCo-TC2 impregnated from toluene solution. Can we further improve the catalytic activity of MoCo-TC2 by improving catalyst dispersion? It is important to answer this question.

We believe that low-rank coals are macromolecular in chemical nature but microporous in physical nature.²¹ Because of its relatively large molecular size (Figure 2.1), the diffusion of MoCo-TC2 molecules into the interior of coal particles through pores may be difficult in 1-MN and toluene. In this context, the superiority of MoCo-TC2 over MoCo-TC3 may be due to better diffusional characteristics of the former, since the only difference between these two precursors lies in the difference between cyclopentadiene (in MoCo-TC2) and pentamethylcyclopentadiene (in MoCo-TC3) ligands. With an attempt to improve the catalyst dispersion on coal by using a swelling solvent, we dissolved MoCo-TC2 in a mixture of THF and toluene (vol: 50:50), with about 5 mL of the binary solvent added per g of coal. This mixture was stirred at 60 °C under N₂ for about 20 h, followed by rotary evaporation of the solvent and vacuum drying at 100 °C for over 2 h. This swelling impregnation method was the most effective, as reflected by considerably higher conversion and higher oil yield with MoCo-TC2 impregnated from THF-toluene compared to the other three methods.

The results in Figure 2.4 indicate that proper dispersion is important for higher performance of MoCo-TC2. Most low-rank coals and bituminous coals swell in suitable solvents such as THF and pyridine. Joseph³¹ first attempted utilizing coal swelling to enhance catalyst dispersion. It has been shown that using proper swelling solvents such as THF and tetrabutylammonium hydroxide for impregnation of metal carbonyls and ATTM on coal could enhance the coal conversion.^{9,31} Combination of the present results with those of Joseph³¹ and Artok et al.⁹ suggests that good swelling solvents probably result in the expansion of the microporous structure and thus enable better dispersion of catalyst precursor molecules.

There are probably four different ways of catalytic hydrogen transfer. First, coal-derived reactive radicals can abstract the free H atoms from catalyst surface. Second, hydrogen transfer from catalyst surface to adjacent or relatively distant sites through surface diffusion or spill-over.

Third, hydrogen transfer from catalyst surface to coal species through liquid-phase or gas-phase transport like a free radical. Finally, catalytic hydrogenation of polycyclic aromatic compounds, which produces in-situ H-donor molecules. This is indirect hydrogen transfer. We believe the first and second pathways are very important in the initial stage of coal liquefaction, and it is these types of H-transfer that makes the catalyst dispersion important for liquefaction of coals, especially low-rank coals which do not melt or physically dissolve in the reaction solvents. Better dispersion of precursor molecules would allow more catalyst particles present at or close to the sites of radical generation, which could lead to more effective dissociation of molecular H_2 and improved hydrogen transfer to coal-derived radicals.

Comparison of MoCo-TC2 with Mixed Metal Carbonyls

In order to evaluate the activity level of the bimetallic precursor relative to the mixture of two corresponding metal compounds, we examined the catalytic activities of $Mo(CO)_6$, $Co_2(CO)_8$, their mixture, and their mixture plus added sulfur under TPL conditions. Using either one alone increased coal conversion by a similar amount. Combination of the two metal compounds gives significantly higher conversion than either $Mo(CO)_6$ or $Co_2(CO)_8$ alone. Adding elemental sulfur further enhances the activity of the resulting catalyst. Figure 2.5 compares MoCo-TC2 (IWI with toluene) with the two metal carbonyls and their mixtures (in 1-MN solution) as catalyst precursors for runs under SSL conditions at $400^\circ C$ for 30 min. It should be mentioned that the metal carbonyls, $Mo(CO)_6$ and $Co_2(CO)_8$ were also used as the starting materials for synthesizing MoCo-TC2 and MoCo-TC3.

Figure 2.6 shows the results of TPL of the coal impregnated with $Mo(CO)_6 + Co_2(CO)_8$ and MoCo-TC2. Both types of precursors were loaded onto coal using the best swelling-loading method: impregnation from their THF-toluene solution, as described above. Using mixed metal carbonyls increased coal conversion from 34 to 71 wt%. Adding elemental sulfur further to $Mo(CO)_6 + Co_2(CO)_8$ enhanced the conversion and oil production to 83 to 41 wt%, respectively. However, the highest conversion, 92 wt%, and the highest oil yield, 47 wt%, were obtained with the single molecular precursor, MoCo-TC2. These results suggest that the composition and structure of precursors are important for achieving high catalytic activity of the resulting dispersed catalyst.

Table 2.4 Effect of Temperature Programming on Liquefaction Using Bimetallic Precursors

Catalyst precursor ^a	Reaction Solvent	Final temp, °C	Reaction Type	Conversion	Products (wt%, dmmf)		
				dmmf wt%	Preasphalt.	Asphaltene	Oil ^b
None	1-MN	400	SSL	32.2	9.4	6.8	16.0
None	1-MN	400	TPL	34.1	8.2	7.0	18.9
MoCo-TC2	1-MN	400	SSL	74.6	18.0	24.2	32.4
MoCo-TC2	1-MN	400	TPL	78.7	19.8	22.0	36.9
Mo(CO) ₆	1-MN	400	SSL	52.3	16.5	10.6	25.2
Mo(CO) ₆	1-MN	400	TPL	52.4	16.4	11.8	24.2
Co ₂ (CO) ₈	1-MN	400	SSL	51.3	15.0	12.6	23.7
Co ₂ (CO) ₈	1-MN	400	TPL	50.2	14.2	12.4	23.6
None	1-MN	425	SSL	46.9	16.4	13.8	16.7
MoCo-TC2	1-MN	425	SSL	68.5	13.9	12.5	42.1
MoCo-TC2	1-MN	425	TPL	81.1	19.5	15.0	46.6
MoCo-TC3	1-MN	425	SSL	61.4	11.9	13.2	36.3
MoCo-TC3	1-MN	425	TPL	76.6	17.5	12.9	46.2
None	Tetralin	400	SSL	71.4	20.6	21.4	29.4
None	Tetralin	400	TPL	79.2	21.1	23.7	34.4
MoCo-TC2	Tetralin	400	SSL	88.1	22.9	21.0	44.2
MoCo-TC2	Tetralin	400	TPL	89.2	25.4	17.4	46.4

a) The bimetallic precursors were loaded onto coal by incipient wetness impregnation from their toluene solution.

b) Including gases.

Table 2.5 Effect of Temperature Programming on Coal Liquefaction Using Bimetallic Thiocubane Precursors MoCo-TC2 and MoCo-TC3**

Catalyst precursor	Solvent for catalyst impregn	Reaction solvent	Reaction condition	Oil + Gas dmmf wt%	Asphalt dmmf wt%	Preasph. dmmf wt%	Tot Conv dmmf wt%
DECS-9 Montana Subbit Coal							
None	400	1-MN	SSL	16.0	9.4	6.8	32.2
None	400	1-MN	TPL	18.9	8.2	7.0	34.1
MoCo-TC2	400	1-MN	SSL	32.4	18.0	24.2	74.6
MoCo-TC2	400	1-MN	TPL	37.0	19.8	22.0	78.7
None	425	1-MN	SSL	16.7	16.4	13.8	46.9
MoCo-TC2	425	1-MN	SSL	42.3	14.9	14.8	72.0
MoCo-TC2	425	1-MN	TPL	46.7	19.5	15.0	81.1
MoCo-TC3	425	1-MN	SSL	36.7	11.9	13.2	61.4
MoCo-TC3	425	1-MN	TPL	46.3	17.5	12.9	76.6
None	400	Tetralin	SSL	29.4	20.6	21.4	71.4
None	400	Tetralin	TPL	34.4	21.1	23.7	79.2
MoCo-TC2	400	Tetralin	SSL	44.1	22.9	21.0	88.1
MoCo-TC2	400	Tetralin	TPL	46.4	25.4	17.4	89.2
DECS-12 Pittsburgh #8 Bitum Coal							
None	400	1-MN	SSL	13.7	20.4	26.8	60.9
MoCo-TC2	400	1-MN	SSL	14.5	27.8	34.3	76.6
MoCo-TC2	400	1-MN	TPL	15.8	28.7	35.4	79.9
None	425	1-MN	SSL	16.3	17.6	16.1	51.4
MoCo-TC2	425	1-MN	SSL	21.8	27.6	23.9	73.3
MoCo-TC2	425	1-MN	TPL	33.1	31.5	23.4	87.9
MoCo-TC2	400	Tetralin	SSL	18.8	32.6	31.0	82.4
MoCo-TC2	400	Tetralin	TPL	21.9	34.2	33.0	89.1

** Impregnated from toluene solution using incipient wetness method.

Figure 2.4 Effect of methods for dispersing MoCo-TC2 in the liquefaction of DECS-9 coal under TPL conditions (200 °C for 15 min, programmed heat-up at 5°C/min to 400 °C, holding at 400°C for 30 min).

Figure 2.5 Comparison of catalytic activity of MoCo-TC2 (IW1 with toluene) with metal carbonyls and their mixture (1-MN solution) for liquefaction of the DECS-9 coal under SSL conditions at 400 °C with 1-MN solvent.

Figure 2.6 Comparison of catalytic activity of MoCo-TC₂ with that of mixed metal carbonyls and the mixture plus added sulfur for liquefaction of the DECS-9 coal (TPL in 1-MN at final temperature of 400 °C). All the catalysts were impregnated onto coal from their THF-toluene solution by the swelling method.

Both the oxide and sulfide of Mo are catalytically active for hydrogenation reactions but the sulfide is superior.¹⁸ When Mo(CO)_6 or $\text{Co}_2(\text{CO})_8$ is used in coal liquefaction, it decomposes and can form metal, metal oxide, and upon reaction with sulfur, metal sulfide. The metal sulfide is the most active for coal hydrogenation, as shown by enhanced conversion upon sulfur addition in previous work⁶⁻⁹ and in the present work (Figure 2.6). The other possible effect of sulfur addition is the formation of H_2S , which could assist in coal conversion. Recent work in this laboratory has shown that using a $\text{H}_2\text{-H}_2\text{S}$ (95:5) mixture increases coal conversion in both thermal and catalytic liquefaction of a subbituminous and a bituminous coal.⁹ Taking these facts into account, the apparent superiority of MoCo-TC2 over the ternary mixture, $\text{Mo(CO)}_6 + \text{Co}_2(\text{CO})_8 + \text{S}$, clearly indicates the advantage of using a proper molecular precursor. The above results suggest that proper binding of Mo, Co, and S in a single molecule could result in a bimetallic sulfide catalyst that has much higher activity than the corresponding mixtures of the Mo and Co compounds plus sulfur. When MoCo-TC2 precursor is loaded onto coal from THF-toluene, adding sulfur had essentially no impact on coal conversion but slightly increased oil yield, as can be seen from Figure 2.6.

In regards to the effects of coal rank, our preliminary data³² suggest that low-rank coals could be better feedstocks for producing oils, as compared to bituminous coals. Using a good catalyst, such as that from MoCo-TC2, allows more efficient production of oils from the low-rank coal under TPL conditions without using H-donor solvent. Studies on the effects of coal rank and operating conditions are now in progress, and the results will be published in due course.

Summary and Conclusions

The work described in this quarterly report provides a fundamental approach to exploring novel bimetallic dispersed sulfide catalysts and optimum conditions for coal conversion. We have synthesized and tested several heterometallic complexes consisting of two transition metals (Mo, Co) and sulfur in a single molecule as precursors to bimetallic dispersed sulfide catalysts for liquefaction of a subbituminous coal. The results show that the structure of the precursors, in particular the ligands bound to the metal species, affect the activity of the resulting catalyst significantly. The nitrogen-containing ligands bound to the metals in the precursor molecule appear to have an adverse effect on the resulting catalyst. Among the M-M' type precursors

tested, Mo-Co thiocubane, $\text{Mo}_2\text{Co}_2\text{S}_4(\text{Cp})_2(\text{CO})_2$ [Cp = cyclopentadiene], designated as MoCo-TC2, produced the best catalyst in-situ.

The performance of the Mo-Co bimetallic catalyst was further enhanced by using temperature programmed conditions. The programmed heat-up serves as an in-situ activation of bimetallic catalyst and coal pretreatment, which contributes to more effective hydrogenation of reactive fragments at high temperature.

The method of dispersion and the type of impregnating solvent also affect the catalyst activity significantly. Both incipient wetness impregnation and swelling impregnation methods were examined. Impregnating MoCo-TC2 onto coal from a swelling solvent system, a binary mixture of THF-toluene, affords the highest conversion (92 wt%) and highest oil yield for runs of DECS-9 subbituminous coal at 400 °C under TPL conditions.

The bimetallic catalyst generated in-situ from MoCo-TC2 is substantially more active than those from mixed metal carbonyls and the mixture of $\text{Mo}(\text{CO})_6 + \text{Co}_2(\text{CO})_8$ plus sulfur. These results indicate that proper binding of Mo, Co, and S in a single molecule could result in a bimetallic sulfide catalyst that has much higher activity than the corresponding mixtures of the Mo and Co compounds plus sulfur.

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Chapter 3

Model Hydrocracking Reactions of 4-(1-Naphthylmethyl)bibenzyl over Monometallic and Bimetallic Dispersed Catalysts

Introduction

Coal liquefaction is an intricate process in which large-sized compounds undergo various reactions. The chemical reactions in liquefaction are believed to involve cleavage of methylene and dimethylene bridges connecting polycyclic aromatic units. Depending on the type of catalyst, major reaction paths may include bond cleavage of larger molecules, hydrogenation of aromatic rings, and the reaction of heteroatoms like oxygen, sulfur and nitrogen with active catalyst sites.

The complexity of coal liquefaction reactions makes it very difficult to study the reaction mechanisms. It is extremely difficult to find optimum reaction conditions for selective bond cleavage. Furthermore, coals from different sources may react differently with different catalysts. We selected therefore the model compound 4-(1-naphthylmethyl)bibenzyl (NMBB), which consists of functionalities that are related to coal structures (1-5). We felt that the use of NMBB enables us to focus on the effects of transition metal-containing catalysts on the cleavage of different C-C bonds and hydrogenation of different aromatic rings in the NMBB structure.

The primary objective of the work in this chapter was to explore the potential of bimetallic dispersed catalysts from heterometallic molecular precursors in their use in model hydrocracking reactions related to coal liquefaction. This chapter describes the use of three types of catalyst precursors in model compound reactions. The first class consists of inorganic salts as MoCl_3 , ATTM and the bimetallic complex $[(\text{Ph}_4\text{P})_2[\text{Ni}(\text{MoS}_4)_2]$. The second is a thiocubane type complex consisting of cobalt, molybdenum and sulfur. The third group consists of metal carbonyls as $\text{Mo}(\text{CO})_6$, $\text{Co}_2(\text{CO})_8$ and their combinations with and without added sulfur. Here we discuss the effects of organometallic (monometallic and bimetallic) as well as inorganic catalyst precursors on conversion and product selectivity, and the influence of the reaction temperature on the product distribution in the model reactions of NMBB.

Experimental Section

Preparation of Catalyst Precursors. The complex $[\text{Ph}_4\text{P}]_2[\text{Ni}(\text{MoS}_4)_2]$ (Ni-Mo) was prepared according to the method described in the literature, based on the procedure of Brunner and Wachter (6). The thiocubane cluster $\text{Cp}_2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_4$ (CoMo-TC2) was synthesized earlier (7) in our laboratory. Samples were stored at -25°C prior to use. All recrystallizations of the homo- and heterometallic cluster compounds were carried out quickly. The crystalline products are stable on exposure to air but decompose slowly in solution. Sulfur and $(\text{NH}_4)_2\text{MoS}_4$ (ATTM) were purchased from Aldrich, $\text{Mo}(\text{CO})_6$, $\text{Co}_2(\text{CO})_8$ from Alfa and the model compound MNBB from TCI America. GC-MS confirmed sufficient purity of MNBB ($> 99\%$) and it was used without further purification.

Model compound reactions. A stainless steel reactor (tubing bomb) with a capacity of 33 ml was loaded with ca. 0.25 g MNBB, 2.11 wt % catalyst precursor and 0.125 g solvent (tridecane). The reactor was purged three times with H_2 and then pressurized with 6.9 MPa H_2 at room temperature for all experiments. A preheated fluidized sand bath was used as heating source and the reactor agitated via an oscillator by vertical shaking of the horizontal micro reactor (about 240 strokes/min.) After the reaction the hot tubing bomb was quenched in cold water and the gaseous products collected in a gas bag for further analysis. The liquid contents were washed with 15 ml CH_2Cl_2 through a low speed filter paper and stored in small glass bottles for qualitative and quantitative GC analysis. All runs were carried out at least twice to confirm reproducibility.

The compounds were identified by capillary gas chromatography-mass spectrometry (GC-MS) using a Hewlett-Packard 5890 II GC coupled with a HP 5971A mass-selective detector operating at electron impact mode (EI, 70 eV). The column used for GC-MS was a J&W DB-17 column; 30-m X 0.25-mm, coated with 100 % phenylmethylpolysiloxane with a coating film thickness of 0.25 μm . For quantification a HP 5890 II capillary GC with a flame ionization detector and the same type of column (DB-17) was used. Both Hewlett-Packard GC and GC-MS were programmed from 40 to 280 $^\circ\text{C}$ at a heating rate of 4 $^\circ\text{C}/\text{min}$ and a final time of 30 min. The response factors of 10 pure compounds were determined. More experimental and analytical details may be found elsewhere (8).

Results and Discussion

Hydrocracking of NMBB. Tables 3.1 and 3.2 show the results of hydrocracking of the model compound NMBB over different catalyst precursors. In the absence of a catalyst, the conversion at 300 °C is only 1 % and increases to about 4 % at 400 °C. The inorganic catalyst precursor ATTM increased the conversion at 350 °C relative to the thermal run by 54 %. A run at 400 °C shows the effect of elevating reaction temperatures. The conversion increased by additional 30 %. Molybdenum trichloride proved to be less effective and gave about 70 % conversion.

Of the catalysts tested, $[\text{Ph}_4\text{P}]_2[\text{Ni}(\text{MoS}_4)_2]$ and $\text{Co}_2(\text{CO})_8+\text{S}$ showed the highest conversion (95 %). Ni-Mo consists of a chain like structure with tetrahedral environment around nickel and molybdenum (Scheme 1).

From the data in Tables 3.1 and 3.2 Ni-Mo is apparently the best precursor among the catalysts tested. A general observation is that the activity of the in situ generated catalysts is smaller at lower temperatures and increases at elevated temperatures. In an attempt to examine the role of bonding between transition metals, we tested the bi-metallic thiocubane-type catalyst $\text{Cp}_2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_4$ (Scheme 2) and different metal carbonyl combinations which may give (after thermal decomposition) similar catalyst composition as Co-Mo-TC2.

There are direct metal-metal bonds between Co-Mo, Co-Co and Mo-Mo, besides the sulfur bridges in CoMo-TC2. The question is, do in situ generated catalysts from catalyst precursors which have metal-metal bonds, show different catalytic behaviour. Table 3.1 shows the superior performance of catalysts containing either Mo, or Co+Mo. Using $\text{Mo}(\text{CO})_6$ alone gave similar results as runs with the mixture of two corresponding metal compounds that can also be found in $\text{Cp}_2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_4$. Among the tested metal carbonyls, $\text{Co}_2(\text{CO})_8$ is less active compared to the thiocubane type catalyst Co-Mo-TC2 and mixed metal carbonyls. A beneficial effect could be observed, when sulfur was added to $\text{Co}_2(\text{CO})_8$. NMBB conversion increased dramatically. Addition of sulfur to $\text{Mo}(\text{CO})_6$ did not improve the convertibility of NMBB, but added sulfur to $\text{Mo}(\text{CO})_6/\text{Co}_2(\text{CO})_8$ gave 10 % higher conversion. Work on the advantage of using different metals in a single catalyst reports the synergistic effect of heterogeneous catalysis. The addition of Co or Ni to MoS_2 -containing precursors increased their catalytic activity considerably. However, little work has been done on comparison of catalytic effects between mixed metal carbonyls, inorganic- and organometallic heteroatomic precursors. Previous work (9,10) reports mainly the mixture of different transition metal salts.

It is known (12-15) that catalyst precursors like metal carbonyls require the addition of sulfur for sufficient activity. The beneficial effect of sulfur addition to hydrogenation reactions was studied on the system molybdenum sulfide and oxide (16). There seems (17) to be consensus that the sulfides of the transition metals are more active in catalytic hydroliquefaction than their oxides. Montano and co-workers (18,19) have emphasized the importance of correct stoichiometry between molybdenum oxides and sulfur in high temperature conversion reactions in order to generate catalytically active MoS_2 particles. Temperatures as high as 350 °C are required for this activation process. In our previous work, it has been demonstrated that the thiocubane CoMo-TC_2 is superior to the mixtures of Mo(CO)_6 , $\text{Co}_2(\text{CO})_8$, and sulfur for liquefaction of a subbituminous coal (8).

Comparison of the results in Tables 3.1 and 3.2 indicates that the thiocubane bimetallic catalysts are not superior to the corresponding mixtures of Co, Mo and sulfur. The rather expensive preparation of the bimetallic catalyst precursors leads to the conclusion that cheaper metal combinations can achieve comparable results. We focused therefore our attention to product selectivity under low severity reaction conditions to study product distribution of NMBB hydrocracking reactions under the influence of homo- and bimetallic catalyst precursors.

Product Distribution

Hydrocracking of NMBB yields three product categories that can be explained by the cleavage of the bonds between the aromatic moieties. The identified products can be classified into hydrocracking, hydrogenation and isomerization products. Those coming from hydrocracking reactions form the major pool of reaction products, followed by hydrogenation and isomerization products.

Figure 3.1 shows the product distribution from catalyst-free reactions. The thermal reaction of NMBB at 300 °C yields only two products, 4-methylbibenzyl (4-MBB) and naphthalene (N). Higher temperature (400 °C) gave enhanced conversion and twice as much products. Besides 4-MBB and N, 1-(naphthyl)-4-tolyl methane (NTM) and tetralin can be found as high temperature products. Generally, increased temperature results in lower selectivity. The ratio of major products in our model reactions over thiocubane catalysts (Figure 3.2) remains similar over a wide temperature range. We can see in Figure 3.2 more 4-MBB than BB and more naphthalene (N) than tetralin. Several studies, including the present work have shown that NMBB tends to undergo cleavage of bond a connecting the naphthyl group to the remainder of the molecule when subjected to a variety of catalysts under a variety of conditions.

Schemes 1-3

Scheme 1: Structure of the bimetallic sulfide $[\text{Ph}_4\text{P}]_2[\text{Ni}(\text{MoS}_4)_2]$.

Scheme 2: Structure of the thiocubane-type catalyst precursor: $\text{Cp}_2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_4$.

Scheme 3: Potential cleavage sites in 4-(1-naphthylmethyl)bibenzyl.

Farcasiu et al. suggested a reaction mechanism in which the first stage consists of the formation of a radical cation. The loss of electron density leads to a weakened a-bond which can then be broken relatively easily. This is in contrast to model studies in which phenyl-containing compounds undergo preferably b-cleavage (5).

In the work of Penn and Wang (5) radical cations were generated in the mass spectrometer under a variety of conditions which had little impact on the bond cleavage pathway. Preference for b-cleavage was observed. It was explained by resonance stabilization of the intermediates formed via bond b cleavage. Both intermediates are resonance stabilized. Thermochemical calculations (20) show that reaction pathway b is 30 kcal/mol lower for both neutral and radical cationic species than pathway α . In contrast, neither of the intermediates resulting from bond a cleavage is stabilized. However, in the presence of a catalyst, the major reaction pathway mainly involves the cleavage of bond a (Scheme 3). These studies indicate that a new decomposition pathway mechanism must be developed to explain the results of bond cleavage involving model reactions on NMBB. The product distribution is different over metal carbonyls (Figure 3.3). The main reaction product is 4-MBB, but the ratio of tetralin/naphthalene depends on the addition of sulfur. Sulfur-free metal carbonyl precursors are relatively better hydrogenating catalysts than sulfur containing metal carbonyls and their combinations. This becomes more apparent in the case of Co+Mo and Co+Mo+S. Sulfur enhances the formation of naphthalene and suppresses the generation of tetralin. In order to get more information about the influence of sulfur on hydrogenation reaction, we carried out experiments with tetralin in tridecane as solvent, with and without added sulfur. A sulfur-free run showed only a negligible amount of naphthalene (naphthalene/tetralin ratio > 0), but the addition of sulfur lead to a substantially higher naphthalene-to-tetralin ratio (0.08).

Table 3.1. Hydrocracking of NMBB over dispersed metal carbonyls and mixed metal carbonyl with and without added sulfur at 400 °C

Reaction temperature (°C)	300	400	400	400	400	400	400	400
Catalyst Precursor	None	None	Mo(CO) ₆	Mo(CO) ₆ + S	Mo(CO) ₆ + Co ₂ (CO) ₈	Mo(CO) ₆ + Co ₂ (CO) ₈ + S	Co ₂ (CO) ₈	Co ₂ (CO) ₈ + S
Products [wt %]								
Cyclohexane							1.1	2.1
Bezene		0.6	0.2	0.7	0.7	0.7		
Toluene		0.3	1.4	0.5	0.4	0.1	0.7	0.8
p-Xylene			0.7	0.2	0.1		0.3	
Tetralin		0.2	17.3	15.1	21.0	11.7	6.8	5.3
Naphthalene	0.4	0.6	13.8	15.3	5.1	19.2	5.4	28.0
2-MTHN			0.8	0.9	0.6	0.8		0.2
1-MTHN			1.8	1.2	2.4	0.9	1.0	0.5
2-MN			0.5	0.4	0.4	0.5		1.2
1-MN			1.7	1.6	0.5	2.0	0.4	3.0
Bibenzyl			7.7	10.5	6.3	10.3	1.0	9.9
2-MBB			0.4					
4-MBB	0.6	1.3	39.8	38.6	38.3	40.7	14.0	44.8
1-NB							0.4	
NTM		0.9						
THNMBB							6.6	
Other-THNMBB							7.9	
Conversion [wt %]	1.0	3.9	86.1	85	75.8	86.9	45.6	95.8

^a Reactor residence time in preheated sand bath 30 min. ^b wt % based on the initial weight of NMBB feed.

Table 3.2: Effect of inorganic and thiocubane-type precursors on hydrocracking reactions^a of NMBB at 300-400 °C

Reaction temperature (°C)	350 ^a	400 ^a	400 ^a	400 ^a	300 ^a	350 ^a	400 ^a	400 ^b
Catalyst Precursor	ATTM	ATTM	MoCl ₃	Ni-Mo	Co-Mo	Co-Mo	Co-Mo	Co-Mo
Products [wt %]								
Benzene		0.7	0.6	4.9			0.5	0.6
Toluene		0.1	1.3	1.0			0.6	0.9
p-Xylene			0.3	0.5		0.3		0.4
Tetralin	6.5	14.2	4.5	8.5	0.5	1.6	6.7	9.4
Naphthalene	14.3	16.9	20.9	23.6	4.0	11.0	24.4	23.2
2-MTHN	0.2			0.4				
1-MTHN	0.8	1.2	0.4	0.8		0.1	0.5	0.6
2-MN	0.1			0.7				
1-MN	1.5	1.7	2.7	2.7		0.6	2.0	2.2
Bibenzyl	3.4	6.3	19.2	6.9	0.5	1.7	4.7	6.0
2-MBB			3.7	0.2				
4-MBB	28.9	45.1	16.4	44.5	6.8	18.2	40.9	44.5
Conversion [wt %]	55.7	86.2	70.0	94.7	11.8	33.5	80.3	87.8

^a Reactor residence time in preheated sand bath: 30 min. ^b 60 min.

Figure 3.1: Yields of products excluding gases for non-catalytic thermal hydrocracking of NMBB at 300-400 °C.

Figure 3.2: Catalytic activity of thiocubane-type catalysts in the temperature range of 300-400 °C for 30-60 min.

Figure 3.3. Catalytic activity of mixed metal carbonyls and the mixture plus added sulfur on hydrocracking of NMBB.

Figure 3.4: Effect of temperature on hydrocracking of NMBB using inorganic catalyst precursors at 350–400 °C for 30 min.

Products found in hydrocracking of NMBB over inorganic catalyst precursors (Figure 3.4) at 400 °C are similar to those found in runs with organometallic precursors. Unlike all other catalysts, the lewis-acid-type complex MoCl_3 gave a different product distribution. MoCl_3 is the only catalyst that cleaved both bond a and b in NMBB with about equal probability. The aggressiveness of MoCl_3 as catalyst precursor is also demonstrated by a relatively larger percentage of isomerization products. The general observation is that low severity reaction conditions lead to higher selectivity. At 350 °C ATTM gives a considerable amount of hydrogenation and isomerization products, whereas the organometallic complex CoMo-TC2 yields only products, coming from hydrocracking and hydrogenation reactions. The latter category of compounds can not be found in a reaction involving $\text{Cp}_2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_4$ at 300 °C.

Summary

For model hydrocracking reactions under the conditions employed, $(\text{NH}_4)_2\text{MoS}_4$ and MoCl_3 converted NMBB predominately into naphthalene and 4-methylbibenzyl. Small amounts of secondary products were formed by hydrogenation and fragmentation of the primary products. Lewis acid-type MoCl_3 catalyst gave lower selectivity to the primary products, with relatively larger amounts of methyltetrahydronaphthalene- and methylnaphthalene-derivatives. In contrast, the bimetallic catalyst precursors $\text{Cp}_2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_4$ and $(\text{Ph}_4\text{P})_2(\text{Ni}(\text{MoS}_4))$ inflict less fragmentation and less hydrogenation of primary cleavage products. $\text{Cp}_2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_4$ converted a substantial amount of starting material even at 350 °C; whereas, a noncatalytic run under the same conditions showed only small conversion. Inorganic and bimetallic catalyst precursors gave similar conversions. Greater product selectivity can be achieved by means of organometallic precursors and low severity reaction conditions. $\text{Mo}(\text{CO})_6$ and $\text{Co}_2(\text{CO})_8/\text{Mo}(\text{CO})_6$ gave similar conversion as the bimetallic catalyst precursors. The addition of sulfur to the combination $\text{Co}_2(\text{CO})_8/\text{Mo}(\text{CO})_6$ gave significant higher conversion but reduced generally the yield of hydrogenation products. The trends observed in this work are consistent with those of literature (21,22) in that certain bimetallic precursors can produce more active catalysts.

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Chapter 4

Hydrogenation of Phenanthrene over Mo-based Bimetallic Catalyst Precursors and Fe-based Thiocubane as Catalyst Precursor

Introduction

The beneficial catalytic effect of multi-component catalytic precursors can be examined via synthesis and testing of a series of organometallic compounds. It may be anticipated that synergistic effects of multi-component catalysts could lead to improved catalytic activity for primary coal liquefaction products like phenanthrene. In the earlier stages of cluster chemistry, the synthetic approach was based on spontaneous assembly. Advances in homometallic transition-metal sulfide chemistry have led to smaller clusters which are fragments of the thiocubane unit. Homometallic "thiocubane" clusters containing an $M_4(\mu_3-S)_4$ core have been known for some time.¹ Heteronuclear thiocubane clusters like $Cp_2M_2S_4$ and $M_2M'_2(\mu_3-S)_4$ have been synthesized. A virtue of this type of compounds is the availability of a wide variety of $M_2S_4^{2+}$ core compounds having sulphur. The importance of MoS_2 -based bimetallic heterogeneous catalysts² and other potential applications of Mo compounds have led to the preparation of various Mo-based heterometallic thiocubanes.³⁻¹⁰ The flexibility of using different ligands provides structural and electronic variations which are not present in the standard catalyst precursor, $(NH_4)_2MoS_4$ (ATTM). One of the main question that arose from catalytic coal liquefaction research is what are the key functions of the catalyst leading to high oil yields and coal conversions. This research is a fundamental study on model compound reaction using bimetallic molecular catalyst precursors.

The primary objective of work described in this chapter was to examine the catalytic activity of novel bimetallic catalysts from organometallic precursors for hydrogenation of polyaromatic compounds. Two different bimetallic complexes $[(C_5H_5)_4P]_2[Ni(MoS_4)_2]$ and $(C_5H_5)_2Mo_2Co_2S_4(CO)_2$, the cluster compound $[C_5H_5FeS_4]_4$ and the inorganic complex $(NH_4)_2MoS_4$ (ATTM) were used as catalyst precursors. We focused our experimental work on the hydrogenation of phenanthrene in the presence of bimetallic catalyst precursors and a solvent. Also, experiments without solvent and without a catalyst were carried out to get baseline data.

Experimental Section

Reagents and Catalyst Precursors

ATTM was purchased from the vendor Aldrich and was used as obtained, without further purification. The organometallic compound with the Co-Mo combination was prepared in our laboratory (MoCo-TC2) as described in Chapter 2. The complexes $[(C_6H_5)_4P]_2[Ni(MoS_4)_2]$ (Ni-Mo) and $[C_5H_5FeS_4]_4$ (Fe4) were prepared according to the methods described below. The organometallic catalyst precursors are stable in the solid state on contact with air and can be stored in the freezer for an unlimited time. The complex Ni-Mo consists of the dianion $[Ni(MoS_4)_2]^{2-}$ core unit and tetraphenylphosphonium as counter ion. Schemes I to VII show the types of the precursors (further described below) and synthetic procedures as well as their structures.

Synthetic Preparation

The organometallic compounds, used in the model compound conversion reactions, contain different transition metals and sulfur in the same molecule. The complexes $[(C_6H_5)_4P]_2[Ni(MoS_4)_2]$, abbreviated as Ni-Mo, and $[C_5H_5FeS_4]_4$, abbreviated as Fe4, were prepared according to the methods described by Muller et al.⁹ and Schunn et al.¹⁰, respectively. The Ni-Mo complex consists of the dianion $[Ni(MoS_4)_2]^{2-}$ core unit and tetraphenylphosphonium as counter ion. The structure can be described as two dimensional chains where the transition metals are surrounded by sulfur in tetrahedral environment. Müller et al.⁹ developed a conceivable way towards bimetallic complexes by precipitating the water soluble core unit with a bulky salt cation. This reaction can also be applied to a whole series of other related bimetallic transition metal thioanions.

The cubane cluster Fe4 has a cubic structure with iron and sulfur in opposite corners and can be prepared easily from the commercially available $[(Cp)Fe(CO)_2]_2$ and elemental sulfur or cyclohexenesulfide.

120 °C, 16 hours

The compound containing Co-Mo belongs to a series of complexes with various functional groups which can be prepared according to a method developed by Brunner and Wachter.³

Synthesis of $[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{Ni}(\text{MoS}_4)_2]$, Ni-Mo. All reactions were carried out under atmospheric conditions. Recrystallizations were carried out as quickly as possible. ATTM, tetraphenylphosphoniumchloride. Nitromethane (CH_3NO_2) and diethylether were purchased from Aldrich. Nickel(II) chloride was found to be available in group resources (obtained earlier from Strem).

ATTM (1.04 g, 4 mmole) was dissolved in 50 ml water and one drop of diluted acetic acid was added. Then 40 ml of an aqueous solution of Nickel(II) chloride $\cdot$ 6H₂O (480 mg, 2 mmole) was added dropwise to the vigorously stirred ATTM containing solution. A black solution was immediately formed which was subsequently filtered through a fast speed filter paper. The literature describes no precipitate in this stage of the reaction. However, a fine black precipitate was observed. More was formed upon standing for a period of time. Dropwise addition of tetraphenylphosphoniumchloride (1.2 g, 3.2 mmole) in 50 ml water gave a dark brown/red voluminous precipitate. It was dried over night in vacuum and redissolved in 250 ml hot nitromethane. Filtration gave a dark red solution which turned brown after the addition of 750 ml cold diethylether. This mixture was stored for 1 hour in a refrigerator and then filtered to yield a red/brown microcrystalline material. Drying in vacuum at 70 °C for 3 days gave 830 mg (0.70 mmole) red/brown product, 35 % (literature yield not described).

The diamagnetic product is like its analogues $[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{M}(\text{MoS}_4)_2]$ (M = Fe, Ni, Zn) soluble in alcohol, chloroform, acetone and nitromethane. However, decomposition occurs after a while in solution. Therefore, all steps involving handling the product in solution should be carried out as quickly as possible. The alternative would be to conduct all experiments in an inert gas atmosphere. The solid material can be stored on air for an unlimited time.

Synthesis of $[(C_5H_5)FeS]_4$, Fe_4 .

In this reaction, all steps were carried out in a nitrogen atmosphere unless otherwise noted. The chemicals cyclopentadienyliron dicarbonyl dimer, sulfur and bromobenzene were obtained from Aldrich and used without prior purification.

About 500 mL toluene were placed in a 1 l flask, sulfur (S_8) (5.2 g, 20.2 mmole) was added and the mixture warmed up to 50 °C. Nitrogen was flushed through the apparatus for 2 hours and then $[(C_5H_5)Fe(CO)_2]_2$ (20 g, 56.5 mmole) was added in small portions to the hot (almost refluxing) toluene solution. The mixture was refluxed for 16 hours and then allowed to cool down to room temperature. Filtration on air and washing with 100 ml hexane gave 15.3 g crude product. Drying in vacuum for 1 hour gave 14.1 g black, microcrystalline material. This material was three times extracted with boiling bromobenzene (250 ml) and filtered to give a brown/black solution in which small crystals were formed readily. The solution was stored overnight at 4 °C on air and the black product collected. The crude, black material was washed with 30 ml cold bromobenzene and subsequently with three 30 ml portions of pentane to give a grey/black glistening microcrystalline product. Drying in vacuum for 3 days at 70 ° yielded 7.6 g (12.4 mmole), 22 % material.

Structure of Fe Thiocubane $[C_5H_5FeS_4]$.

The functional groups, as shown in scheme IV $[C_5H_5FeS_4]$, consists of an elongated tetrahedron of iron atoms with a sulfur atom over each face and a cyclopentadienyl group projecting from each corner.¹¹ The overall symmetry of the molecule is D_{2d} . The interiron bonds have a length of 2.618 Å and 2.644 Å. The different bond lengths are possibly due to crystalline forces caused by different hybrid character of the orbitals used in forming the interiron bond.¹² The average iron-iron bond is greater than those found in the carbon-bridged complexes, but lies in the center of the range found for sulfur-bridged Fe-Fe bonds. The long edges of the iron tetrahedron are 3.368 Å in length and are not interiron bonds. There are two classes of Fe-S bonds realized, those paralleling the long axis of the tetrahedron averaging 2.256 Å in length and those bridging the interiron bonds averaging 2.206 Å. The average Fe-Cp distance of 1.757 Å is somewhat longer than the value found in ferrocene,¹³ but agrees very well that of 1.75 Å found in $[(Cp)Fe(CO)_2]_2$.¹⁴ Other tetrahedral complexes are known and also based on transition-metal ligand cubic structures.¹⁵ $[(C_5H_5)FeS]_4$ is stable towards oxygen and water in the solid state but slowly decomposes in solution. The solubility in organic solvents is quite low and the tetrameric nature was discovered only as a result of the crystal structure analysis. The compound is diamagnetic.

Scheme I

Organometallic Catalyst Precursors

Abbreviation	Molecular Formula	Structure type
Ni-Mo	$[(C_6H_5P)_2[Ni(MoS_4)_2]$	Sulfide complex
Fe4	$[(C_5H_5)FeS]_4$	Thiocubane type
Co-Mo	$Cp_5Co_2Mo_2(CO)_2S_4$	Thiocubane type
ATTM	$(NH_4)_2MoS_4$	Sulfide complex

Scheme II

SYNTHESIS OF THE BIMETALLIC SULFIDE $[(C_6H_5)_4P]_2[Ni(MoS_4)_2]$

1) Dianion:

Scheme III

STRUCTURE OF THE BIMETALLIC INORGANIC
SULFIDE $[(C_6H_5)_4P]_2[Ni(MoS_4)_2]$

(Dianion)

Scheme IV

STRUCTURE OF THE CLUSTER
 $[(C_5H_5)FeS]_4$

Scheme V

SYNTHESIS OF THE CATALYST PRECURSORS

- CO

Scheme VI

STRUCTURE OF THE BIMETALLIC THIOCUBANE
Co-Mo

Scheme VII

SYNTHESIS OF THE CATALYST PRECURSOR

Thiocubane type

Hydrogenation Reaction Conditions

All reactions were carried out in a 33 ml tubing bomb microautoclaves in a temperature controlled fluidized sandbath at a constant vertical stroking rate of 246/min. over a period of 30 min. to 1 hour. Each reactor was loaded with approximately 1 g of phenanthrene and 1 g solvent (tridecane). The concentration of the catalyst precursors was in the range of 0 to 2.11 wt %, based on the metal. Reaction temperatures were kept between 375 and 425 °C at a hydrogen pressure of 6.9 MPa. The reactors were quenched rapidly with a cold water bath and cleaned before venting. The contents were washed with either 15 ml toluene or 15 ml methylene chloride through a fast speed filter paper and collected in a vial. The starting material phenanthrene and its converted products are quite soluble in both solvents. The residue was dried for three days in vacuum at 100 °C and kept in small glass bottles. Each reaction was carried out twice to confirm reproducibility. These results are preliminary.

The total conversion is the sum of mol % of products, based on starting material (phenanthrene). The collected products were analyzed by quantitative (GC) and qualitative (GC-MS) chromatography, using 5890 Hewlett Packard systems fitted with a 30 m x 0.25 mm i. d. capillary column with 50 % phenylmethylsilicone stationary phase with a film thickness of 0.25 mm. Helium was used as a carrier gas. The data acquisition and processing were controlled through a computer-aided system. The column temperature was programmed from 40 °C to 280 °C at a rate of 4 °C/min. while the mass spectrometer was operated at 70 eV.

Results and Discussion

Noncatalytic Hydrogenation

To compare the effectiveness of the catalyst precursors, catalyst-free model reactions were conducted under the same condition as the experiments where catalysts had been employed. Product analysis showed only small amounts of converted starting material. They consist of hydrogenated phenanthrene derivatives with 9,10-dihydrophenanthrene (DHP) and 1,2,3,4-tetrahydrophenanthrene (THP) as main products. DHP was preferably formed and found in 9 times higher quantities than THP. No hydrocracking, or isomerization products of phenanthrene could be detected. The overall conversion (based on phenanthrene) was 7.2 %.

Hydrogenation with Catalyst

Tables 4.1-4.4 show the result of the hydrogenation of phenanthrene with various catalysts. Scheme VIII shows an example of product distribution from catalytic hydrogenation. The reactions were carried out to determine effective catalyst precursors concentrations for optimum phenanthrene conversion. Catalyst concentration of under 0.5 wt % metal in the case of ATTM and Ni-Mo increased the yield of hydrogenated products significantly. Both catalysts promote comparable amounts of conversion products. A metal concentration of 2.11 wt % in the precursors leads to a considerably higher rate of conversion, whereas Ni-Mo shows a higher performance than ATTM or Co-Mo. Both bimetallic catalyst precursors exhibit better capabilities as conversion agents than the monometallic inorganic precursor ATTM, even though the thiocubane Co-Mo catalyst's performance ranks behind that of Ni-Mo. Another thiocubane type catalyst precursor Fe₄ with related structure to Co-Mo does not enhance phenanthrene conversion, despite its organometallic nature with four iron atoms as core units. The performance of Fe₄ is comparable to that of a catalyst-free run. The above results indicate that ligand and metal species affect the activity of the resulting catalyst significantly. Ni-Mo, which has no direct metal-metal bond, has a beneficial effect on the rate of conversion and is superior to Co-Mo, which possesses intermetal bonds. This finding is in contrast to coal liquefaction experiments wherein Co-Mo shows better performance.

Effect of Temperature in Hydrogenation Reaction

In regards to the influence of the temperature profile on the catalyst activity, we compared the runs of several catalyst precursors at temperature intervals of 25 °C in the important temperature range of 375 °C to 425 °C. One experiment with the catalyst precursor ATTM was conducted at 300 °C and showed no activity at all. With the exception of Ni-Mo, the other catalysts reached their optimum activity at a temperature of 400 °C. The initial step in primary coal liquefaction is the thermally initiated fragmentation followed by the reaction of fragments with hydrogen donors, as gas-phase H₂ and hydrogen in donor solvents. The fragments can recombine or crosslink to form insoluble material and decrease overall conversion into hydrogenated and hydrocracking products. Relatively higher temperatures can destabilize the sensitive balance between coal or model compound conversion and the formation of high molecular weight material. In coal liquefaction, it is important to find the right temperature to match the rate of radical production with the system's ability to cap the generated free radicals.¹⁶

Table 4.1 Hydrogenation of Phenanthrene Using Monometallic ATTM Precursor

Catalyst Metal concentration	ATTM	None	ATTM	ATTM
	0.37 wt % Mo		0.37 wt % Mo	3.67 wt %
Reaction time	30 min.	60 min.	60 min.	60 min.
Temperature [°C]	300	425	425	425
Phenanthrene (recovered) [%]		89.7	59.2	47.0
9,10-DHP [%]		6.5	17.2	9.5
1,2,3,4-THP [%]		0.7	18.0	18.3
sym-OHA [%]				
sym-OHP [%]			1.1	6.4
cis-unsym-OHP [%]			0.9	0.8
trans-unsym-OHP [%]			1.0	2.0
Total conversion [%]	0.0	7.2	38.1	36.9

Table 4.2 Hydrogenation of Phenanthrene Using Ni-Mo Catalyst Precursor

Catalyst	[(C6H5)4P]2- [Ni(MoS4)2]	[(C6H5)4P]2- [Ni(MoS4)2]	[(C6H5)4P]2- [Ni(MoS4)2]	[(C6H5)4P]2- [Ni(MoS4)2]
Metal concentration	2.11 wt % Ni+Mo	2.11 wt % Ni+Mo	0.16 wt % Mo 0.21 wt % Ni+Mo	1.68 wt % Mo 2.11 wt % Ni+Mo
Reaction time	60 min.	60 min.	60 min.	60 min.
Temperature [°C]	375	400	425	425
Solvent	Tridecane	Tridecane	Tridecane	Tridecane
Phenanthrene (recovered) [%]	31.7	19.9	55.2	36.2
1,2,3,4-THP [%]	12.0	11.6	15.6	4.8
9,10-DHP [%]	19.7	4.5	14.6	23.3
sym-OHA [%]	4.9		5.7	
sym-OHP [%]	9.6	9.7	5.0	20.0
trans-unsym-OHP [%]	3.5	4.2	0.7	2.3
cis-unsym-OHP [%]	3.2	1.8	0.8	6.7
Total Conversion [%]	52.7	37.3	36.7	57.0

Table 4.3 Hydrogenation of Phenanthrene Using Co-Mo Catalyst Precursor

Catalyst	Cp ₂ (CO) ₂ Mo ₂ Co ₂ S ₄	Cp ₂ (CO) ₂ Mo ₂ Co ₂ S ₄	Cp ₂ (CO) ₂ Mo ₂ Co ₂ S ₄
Metal concentration	2.11 wt % Co+Mo	2.11 wt % Co+Mo	2.11 wt % Co+Mo
Reaction time	60 min.	60 min.	60 min.
Temperature [°C]	425	400	375
Solvent	Tridecane	Tridecane	Tridecane
Phenanthrene (recovered) [%]	25.50	20.50	21.20
1,2,3,4-THP [%]	15.70	12.90	8.50
9,10-DHP [%]	7.30	11.40	14.80
sym-OHA [%]	1.30	2.30	0.70
sym-OHP [%]	8.90	15.50	5.80
trans-unsym-OHP [%]	2.50	4.10	1.80
cis-unsym-OHP [%]	1.20	2.90	1.90
Total Conversion [%]	36.70	46.50	33.30

Table 4.4 Phenanthrene Hydrogenation Using Fe Thiocubane Catalyst Precursor

Catalyst	Cp ₄ Fe ₄ S ₄	Cp ₄ Fe ₄ S ₄	Cp ₄ Fe ₄ S ₄
Metal concentration	2.11 wt % Fe	2.11 wt % Fe	2.11 wt % Fe
Reaction time	60 min.	60 min.	60 min.
Temperature [°C]	375	400	425
Solvent	Tridecane	Tridecane	Tridecane
Phenanthrene (recovered) [%]	73.9	58.4	54.1
1,2,3,4-THP [%]	1.4	0.8	1
9,10-DHP [%]	3.3	3.2	5.1
sym-OHP [%]	1.3	0.9	0.8
cis-unsym-OHP [%]			
trans-unsym-OHP [%]			
Total conversion [%]	5.8	4.8	6.8

Scheme VIII

Effect of Catalyst Precursor Type

The bimetallic catalysts Ni-Mo and Co-Mo, the thiocubane precursors Fe₄ and the inorganic complex ATTM were used in reactions under various conditions with phenanthrene. As shown in tables 1-4 all catalysts promote hydrogenation of phenanthrene to form mainly DHP and THP. Fragmentation products could not be detected, due to the relatively low¹⁷ reactivity of phenanthrene. Hydrogenation products form the major pool of products. However, the hydrocracking ability of our catalysts is well established through experiments, reported in earlier studies¹⁸. All catalysts showed basically no effect at 375 °C - 425 °C for breaking C-C bonds in the polycyclic aromatic phenanthrene molecule. Instead, the conjugated double bonds are partially reduced and isomerization of phenanthrene to anthracene takes place on a small scale. Benzene-like units in all phenanthrene derivatives are preserved, in accordance to the great stability of conjugated basic aromatic systems. The main products DHP and THP show up in much higher quantities than sym- and unym-octahydrophenanthrene (sym-OHP and unym-OHP). It is plausible to assume a stepwise reduction mechanism¹⁹ in which addition of hydrogen to the starting material phenanthrene gives first DHP, followed by THP and OHP. Finely divided nickel is known in the literature²⁰ as a good hydrotreating agent. Elevated temperatures and high pressure can even reduce benzene to cyclohexane reversibly. The first step in hydrogenation is the absorption of hydrogen on the surface of our Ni-, Co- and Mo- containing catalysts. In the second step, the relatively weakly bonded hydrogen is being transferred to cap the radical sites of our model compound to form the observed hydrogenated products.

ATTM promotes the formation of DHP and THP, whereas the yield of OHP is relatively small. A higher percentage of OHP is achieved by a higher metal concentration. This may be accomplished by a greater catalyst surface area to reduce more DHP to THP and finally to OHP. The sym-OHP derivative is favored over cis- and trans-unsym-OHP, which occur in about the same ratio and can be related to specific catalyst capabilities. Low Ni-Mo concentrations effect about equal ratios of DHP and THP. A catalyst-free run produced a great excess of DHP. Increased metal concentration gives higher yields of DHP at 375 °C and 425 °C. The catalyst Co-Mo converts phenanthrene at 400 °C at about the same percentage to DHP and THP. Higher temperatures (425°C) favor the production of DHP, whereas relatively milder reaction conditions (375 °C) give more THP. Both bimetallic catalysts show no identical pattern in product selectivity. Therefore each catalyst surface must have certain reactive sites to generate specific products. Other catalysts with new ligand environments will be tested to optimize the rate of conversion and product

selectivity. Also, new model compounds will be introduced, since the reactivity of phenanthrene is relatively low.

Summary

It was found that the structure and the ligands in the model complexes affect the activity of the resulting dispersed catalyst significantly. The optimum reaction at a pressure of 6.9 MPa hydrogen gas varied for different catalysts. The bimetallic catalysts generated in situ from the organometallic precursor are more active than monometallic catalysts like ATTM and the thiocubane type cluster Fe_4 . Main products are hydrogenated phenanthrene derivatives, like DHP, THP, sym-OHP, cis- and trans-unsym-OHP with minor isomerization products such as sym-OHA. Our results indicate that other transition metal and ligand combinations in the organometallic precursors and the use of another model compound could result in substantially higher conversion activity.

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Chapter 5

Hydrotreatment of 4-(1-Naphthylmethyl)bibenzyl in the Presence of Inorganic and Organometallic Fe Catalyst Precursors and Sulfur

Introduction

Direct coal liquefaction is facilitated by use of catalysts, to aid in the initial depolymerization of the coal macromolecule or in the hydrotreatment of the primary products of reaction, or both. Over the years compounds of virtually every element that might be suspected of possessing catalytic activity have been tested as potential liquefaction catalysts. Iron compounds often appear to be less active than compounds of some other elements, notably molybdenum, when tested under comparable conditions. Despite that, a variety of reasons indicate that iron-based catalysts offer many advantages for liquefaction processing. These advantages include low cost; ready availability; the potential of use as "once through" catalysts, obviating the need for catalyst recovery and recycle operations; and reduced environmental concerns on disposal. As a result, the past decade has witnessed an extraordinary research effort on iron-based catalysts for direct liquefaction.

The intervention of the catalyst in the early stages of coal decomposition and dissolution is likely to be facilitated if the catalyst is well dispersed over the surface of the coal particles. Catalyst activity may also depend on particle size. The substance generally considered to be the most active iron-based liquefaction catalyst is the non-stoichiometric sulfide pyrrhotite, Fe_{1-x}S .¹ Many iron-containing materials have been tested as catalysts, including red mud,²⁻⁴ iron(III) oxide^{5,6} and aerosols of iron oxides,⁷ iron(III) oxyhydroxide,^{5,8} sulfated iron (III) oxide,^{5,9,10} sulfated iron(III) oxyhydroxide,⁸ and a variety of other oxide and hydrous oxide phases.¹¹ Since the iron oxides and sulfides are not soluble in common solvents, possibly making it hard to achieve a good dispersion of small particles, so-called catalyst precursors can be used instead. A catalyst precursor is a compound that may not possess much, if any, catalytic activity itself, but transforms to an active catalyst under the reaction conditions of interest. A remarkable variety of iron compounds has been evaluated in recent years as prospective catalyst precursors. These include iron(III) nitrate,^{12,13} iron(II) sulfate,^{2,4,13,14} iron(III) sulfate,¹³ iron(III) chloride,¹⁵ iron(II) oxalate,¹⁶ iron(III) acetate,¹⁷ iron(III) acetylacetonate,^{16,18} iron(II) naphthenate,¹⁸ iron(II) stearate,¹⁸ iron pentacarbonyl,^{3,10,16,19,20} triphenylphosphine-

substituted iron carbonyls,²¹ and various binuclear organometallics^{22,23} such as $(C_5H_5)_2Fe_2(CO)_4$ and $(\mu-S_2)Fe_2(CO)_6$. An ingenious effort has also been made to use an iron-loaded coal as a catalyst for reactions with untreated coals.²⁰

It has been known for some time that iron oxides are not as effective in catalyzing hydrogenolysis reactions as iron sulfides.²⁴ Thus when iron compounds not containing sulfur are used as catalysts or catalyst precursors, attempts are made to sulfide the material before use. Elemental sulfur serves as a sulfiding agent.^{6,25,26} Other sulfur compounds also work in this application; sodium sulfide is an example.^{2,15} A useful review of the phase relationships in the Fe-O-S system is available.²⁷ Iron sulfide in combination with hydrogen sulfide as liquefaction catalyst has also been reviewed.²⁸

Because coals have ill-defined structures and reactions of coals can lead to large numbers of products even under mild conditions, fundamental work in coal chemistry has customarily relied on the use of model compounds. These materials have known structures and, ideally, their reactions lead to a small number of products. This simplifies both the analyses of the products and attempts to understand reaction mechanisms or pathways. Recently 4-(1-naphthylmethyl)bibenzyl (NMBB) has become a popular model compound for studying coal-like reactions, particularly under liquefaction conditions.^{4,5,11,18,21,29-33} The structure of NMBB is

An intriguing feature of the NMBB structure is the presence of five different $C_{ar}-C_{al}$ or $C_{al}-C_{al}$ bonds. Following the system established by earlier workers, these bonds are denoted as **a** through **e** in the structure shown above. (Some authors refer to this compound as naphthylbibenzylmethane and use the abbreviation NBBM; the system of labeling the bonds remains the same.)

Experimental Section

Materials. NMBB was purchased from TCI America. A sample of superfine iron oxide (SFIO) was provided by Mach I, Inc., King of Prussia, Pennsylvania. All other compounds—iron catalyst precursors, solvents and sulfur—used in this study were purchased from commercial sources and were used without further treatment or purification.

Reaction Conditions. Reactions were conducted in 33 mL 316-stainless steel microautoclaves (tubing bombs) at 400°C for 30 min (in the fluidized sandbath). The reaction time of 30 min includes the reactor heat-up time of about 6 min. In a typical experiment, the reactor was loaded with 0.78 mmol NMBB, a given amount of catalyst precursor (2.11 wt% Fe, based on NMBB), and 0.78 mmol n-tridecane solvent. The reactor was purged three times with hydrogen and then pressurized with hydrogen to 6.9 MPa at ambient temperature. A preheated fluidized sand bath was used as the heat source. The horizontal reactor was agitated vertically at ≈ 240 cycles/min to provide mixing. After the reaction, the hot reactor was quenched in cold water. The liquid products were washed from the reactor with 15 mL dichloromethane through a filter paper for subsequent analysis of the filtrate. The reactors were cleaned by treating in a base bath (KOH in aqueous isopropanol), followed by water and ethanol washing and drying prior to the subsequent reaction.

Analyses. The products were identified by gas chromatography / mass spectrometry (GC/MS) using a Hewlett-Packard model 5890 II GC coupled with a Hewlett-Packard model 5971A mass selective detector operating in the electron-impact mode at 70 eV. The column was a 30 m long, 0.25 mm diameter J&W type DB-17 column coated with 50% phenyl-50% methylpolysiloxane at a thickness of 0.25 μm . For quantification of the products, a Hewlett-Packard model 5890 II GC was used, with the same DB-17 column and a flame ionization detector. Both GC and GC/MS were temperature-programmed from 40 to 280°C at 4°C/min with a final holding time of 15 min. The response factors for ten of the products were determined using pure compounds. Because of the small amount (250 mg) and high molecular weight of NMBB used for reaction, its recovery was not always satisfactory. Conversions were determined by summing the amounts of reaction products recovered.

Results and Discussion

Baseline Reaction without Iron Catalyst or Sulfur Addition. Reaction of NMBB without added catalyst provides a baseline for comparison of all of the catalytic reactions. Results are shown in Table 5.1. Naphthalene and 4-methylbibenzyl are the main products. They arise from hydrocracking at bond **a**. A small amount of tetralin forms, indicating that even in the absence of catalyst, some utilization of gaseous hydrogen occurs. The low conversion observed in this reaction, 3.9%, agrees well with other reported values in the literature.^{18,29,30} A temperature of 400°C seems to be the threshold needed for thermal reactions of NMBB, since it does not thermally react at temperatures <400°C.³¹ Previous investigators have reported cleavage at bond **a**, as indicated, for example, by identification of 4-methylbibenzyl among the reaction products.^{18,29,30} However, it has also been reported that, at least for temperatures $\geq 410^\circ\text{C}$ the dominant cleavage in thermal runs is at bond **d**.^{29,30} Cleavage at this site would explain the observed formation of naphthyltolylmethane as a product.¹⁸ While our results from catalytic reactions support the pathway via bond **a**, we also found naphthyltolylmethane as a product in non-catalytic reactions at 400°C for 30 min (Table 1) or 60 min. Naphthyltolylmethane is believed to be formed via non-catalytic cleavage of bond **d**. Such a product was not found in catalytic reactions. We have no evidence from any of our reactions for extensive demethylation accompanying the hydrogenolysis of NMBB.

Effects of Iron-Containing Precursors on Hydrocracking of NMBB. Several iron-containing catalyst precursors—ferrocene, iron(II) sulfate, and SFIO—were tested to study the impact of sulfur addition on the catalytic reactions of NMBB with hydrogen at 400°C. To establish a baseline for evaluating the effect of added sulfur, control reactions were performed in the absence of sulfur. Results are shown in Table 5.1. It should be noted that the conversion values reported here are based on the mass of recovered products, and may be lower than true values. The true NMBB conversion values should be $\geq$ sum of molar yields of naphthalene, methylnaphthalene, tetralin, naphthyltolylmethane, benzylnaphthalene (if any), and tetrahydro-NMBB because these products correspond to the starting material in a stoichmetric (molar) ratio of 1:1. The runs reported in Table 5.1 and Figure 5.1 with or without added sulfur were conducted using the reactors that have not been exposed to sulfur. The effect of added sulfur without Fe and the influence of residual wall catalytic effect of the "sulfided reactors" are discussed later in this paper.

Table 5.1. Effect of iron catalyst precursors on hydrocracking of NMBB at 400°C.

Catalyst Precursor ^a	None	Cp ₂ Fe	Cp ₂ Fe+S	FeSO ₄ ·7H ₂ O	FeSO ₄ ·7H ₂ O +S	Superfine Fe ₂ O ₃	Superfine Fe ₂ O ₃ +S
Conversion (wt%) ^b	3.9	15.8	9.6	3.7	23.9	27.1	78.2
Product (mol %) ^c							
Toluene	1.0	1.6	1.1		1.3	1.3	1.9
p-Xylene						0.3	0.7
Tetralin	0.6	0.4	0.3		0.6	3.0	4.0
Naphthalene	1.4	13.8	10.3	4.5	24.0	16.4	64.1
1-Methylnaphthalene		5.6	0.5		1.5		5.8
2-Methylnaphthalene							1.4
Bibenzyl		2.6	0.6	0.6	2.5	1.0	8.9
4-Methylbibenzyl	2.0	9.4	7.4	2.6	19.1	17.4	59.6
NTM ^d	1.2						
Tetrahydro-NMBB						7.3	5.5

a) When sulfur was added, the atomic ratio of S:Fe was 1:1.

b) Conversion is the sum of yields of recovered products expressed in wt%.

c) Mol% based on the starting material, NMBB.

d) Naphthyltolylmethane

In terms of NMBB conversion, the order of catalyst activities was SFIO > ferrocene >> iron(II) sulfate. Although the observed activities differed in each case, in all three reactions naphthalene and 4-methylbibenzyl dominated the product slate. Under these conditions, bond **a** was the preferred site for hydrocracking. Toluene, produced likely by cleavage of bond **d**, and bibenzyl, from cleavage of bond **b**, represented minor products in these reactions. Reaction in the presence of ferrocene showed formation of some methylnaphthalene, the other product from cleavage of bond **b**.

Figure 5.1. The effect of catalytic hydrocracking of NMBB at 400°C for 30 minutes.

These results agree with previous observations. Iron-catalyzed reactions appear to show high selectivity for cleavage of bond **a**,⁵ with naphthalene and 4-methylbibenzyl consistently being major products.¹¹ In iron-catalyzed reactions, cleavage of bond **b** is limited.⁵ Reaction at site **d** appears unaffected by added catalyst, the products from cleavage at **d** being in about the same amount from catalytic or non-catalytic reactions.^{5,21} The apparent resistance of the weak bond **d** to cleavage in these reactions derives from the fact that nonstoichiometric iron sulfides are very selective for cleavage of $C_{ar}-C_{al}$ bonds, particularly between polycyclic aromatic systems and aliphatic carbon atoms, even in the presence of weak $C_{al}-C_{al}$ bonds.⁵ Supporting evidence comes from reactions of 1,2-dinaphthylethane, in which ring hydrogenation was favored relative to cleavage of the $C_{al}-C_{al}$ bond.³⁴

In the reactions with ferrocene and SFIO, tetralin appeared as a minor product. Tetralin would arise from hydrogenation of naphthalene. Its formation shows that the hydrocracking reactions were accompanied by some hydrogenation, though under these conditions hydrocracking dominates. The hydrogenation activity of the three catalyst precursors, deduced from the amount of tetralin formed, is SFIO > ferrocene > iron(II) sulfate. This parallels the order of activity for conversion of NMBB. The small contribution of tetralin to the product slate is consistent with iron sulfides having low activity for hydrogenation of aromatic rings.¹ For example, iron sulfides are much less effective at ring hydrogenation than is metallic iron.³⁵ No evidence was observed for hydrogenation of any of the reaction products with single aromatic rings. This is consistent with the general observation of naphthalene rings being more easily reduced than benzene rings (at least for reduction to tetralin).^{36,37} The hydrocracking of naphthalene proceeds via reduction to tetralin, followed by isomerization to methylindan, and subsequent bond cleavage in the reduced ring.³⁸ We found no evidence for indans among the reaction products, suggesting that, even had longer reaction times been employed, naphthalene hydrocracking is unimportant in these systems.

Comparison of the products of non-catalytic reaction and reaction in the presence of iron(II) sulfate shows that, even though the conversions are similar, the addition of the iron(II) sulfate has affected the product distribution. With added iron(II) sulfate, reaction occurs dominantly at bond **a**, forming naphthalene and 4-methylbibenzyl, and to a lesser extent at bond **b**, to form bibenzyl. No other bonds appear to be affected in the reaction with iron(II) sulfate under these conditions. The non-catalytic reaction, at the same level of conversion, shows hydrocracking at bonds **a** and **d**. These results demonstrate that the

added iron(II) sulfate intervenes by affecting the hydrocracking pathways at the molecular level, even though it has no macroscopic effect in terms of enhancing conversion. Essentially, iron(II) sulfate shuts down the reaction pathway via bond **d**, and turns on a new pathway via bond **b**. A further point of difference lies in the utilization of gaseous hydrogen; some hydrogenation product (tetralin) forms in the non-catalytic reaction, but, interestingly, none in the reaction with added iron(II) sulfate.

Experiments using SFIO yielded only moderate conversion (27.1%), even at 400°C. Hydrocracking at bond **a** is the dominant reaction pathway. Hydrogenation of naphthalene ring occurs in this case, giving 7.3% tetrahydro-NMBB. Cleavage of bond **d** occurs to a limited extent, as shown by formation of some toluene. This was not observed in reactions with iron(II) sulfate, which gave much lower conversion. It seems to agree with the general concept that as one uses a more active catalyst, the catalyst itself is less selective in its action.³⁹

The addition of sulfur to reactions with added iron compounds gives results markedly dependent on the specific iron compound used in the reaction. The most significant enhancement of conversion was obtained in reactions of SFIO with added sulfur. Compared to reaction without sulfur, the conversion jumps by 51 percentage units, from 27.1% to 78.2% (Table 5.1). As was the case without sulfur addition, naphthalene and 4-methylbibenzyl dominate the product slate, showing that hydrocracking at bond **a** occurs in greatest extent. Toluene again appears as a minor product, from cracking at **d**. Methylnaphthalene and bibenzyl are minor products from scission of bond **b**. Tetralin remains a minor product, showing that even when the conversion has nearly tripled relative to reaction without added sulfur, hydrocracking is much more important than hydrogenation. In this case, yield of tetrahydro-NMBB (5.5%) is slightly higher than that of tetralin (4.0%). 2-Methylnaphthalene also occurs among the products. It could be formed from the cleavage at the bond **b** in 4-(2-naphthylmethyl)bibenzyl, which has been observed in a very small amount in the reaction system.⁴⁰ 2-Methylnaphthalene could also be formed from isomerization of 1-methylnaphthalene.

The addition of sulfur also enhances conversions obtained with added iron(II) sulfate, although conversion even with added sulfur, 23.9%, is less than that obtained with SFIO and no added sulfur. As in the case of SFIO+sulfur, reaction with iron(II) sulfate and sulfur show the clear dominance of hydrocracking at bond **a**. In fact, the product slates from SFIO+sulfur and iron(II) sulfate + sulfur are generally similar. The most notable

difference is the lack of evidence for isomerization (i.e., formation of 2-methylnaphthalene) in the iron(II) sulfate + sulfur system. In contrast to reaction without added sulfur, a small amount of hydrogenation (formation of tetralin) takes place in the iron(II) sulfate + sulfur reactions.

When ferrocene is used as the catalyst precursor, the addition of sulfur actually depresses the conversion. The conversion dropped from 15.8% to 9.6%. Although we do not yet have a good explanation for this behavior, it is not an isolated instance of the unusual effects of organometallic catalyst precursors, particularly those containing the cyclopentadienyl ligand. We also observed a decrease in NMBB conversion upon sulfur addition to cyclopentadienyl diiron tetracarbonyl, $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ (where Cp = cyclopentadienyl).⁴¹ In a companion paper in this issue, we show the effects of using the bimetallic thiocubane-type precursor $\text{Cp}_2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_4$ for hydrotreatment of dibenzothiophene.⁴² At comparable catalyst loadings, conversions of dibenzothiophene with this thiocubane were lower, by factors of 2–6, than those obtained with all other molybdenum-containing catalyst precursors tested.

Effects of Sulfur Addition Without Iron Catalysts. Table 5.2 and Figure 5.2 summarize results obtained for the addition of sulfur to NMBB reactions but without iron compounds being added. Conversion of NMBB clearly depends on the level of sulfur addition (Figure 5.3). At 1.2 wt% (based on NMBB) sulfur, the conversion, 26.1 wt%, compares well to those obtained in reactions with SFIO and with iron(II) sulfate + sulfur, which were 27.1 and 23.9 wt%, respectively. 4-Methylbibenzyl and naphthalene dominate the product slate, again demonstrating high selectivity for NMBB cleavage at bond a. These were also the dominant products with the SFIO and iron(II) sulfate + sulfur systems.

Table 5.2. Effect of sulfur addition on hydrocracking of NMBB at 400°C without iron catalysts.

Sulfur Addition	None	1.2 wt% S	3.4 wt% S	None	None
Reactor History	Unsulphided reactor ^a	Unsulphided reactor ^a	Unsulphided reactor ^a	Sulphided reactor ^b	HCl treated reactor ^c
Conversion (%)	3.9	26.1	82.5	23.0	11.6
Product (mol %)					
Toluene	1.0	1.4	4.9	1.0	1.0
Tetralin	0.6	0.8	2.9	0.8	0.4
Naphthalene	1.4	24.8	74.4	19.1	10.8
1-Methylnaphthalene		1.7	9.5	0.8	0.7
2-Methylnaphthalene			7.8		
2-Methyltetralin			0.4		
NTM ^b	1.2				
Bibenzyl		2.4	42.5	1.0	1.2
4-Methylbibenzyl	2.0	22.1	32.3	18.3	9.7
TH-NMBB				2.7	

a) Unsulphided reactor refers to the reactor that was used in previous experiments without added sulfur.

b) Sulphided reactor refers to the reactor that was used in a previous experiment with 3.4 wt% added sulfur.

c) HCl treatment was performed on the sulphided reactor at room temperature.

Figure 5.2. The effect of sulfur on NMBB hydrocracking product distribution at 400°C for 30 minutes.

Figure 5.3. The effect of sulfur on NMBB conversion in non-catalytic experiments.

It should be noted that significant amounts of benzothiophene- type sulfur-containing compounds were observed by Darab et al.⁴³ in the reaction of NMBB in the presence of sulfur with and without an iron catalyst. However, we have confirmed from our GC and GC-MS data that such sulfur compounds, if any, were negligible under the conditions employed. The possible reason for this discrepancy could be that the sulfur/NMBB mol ratio used in the work of Darab et al.⁴³ is much higher (0.31 mmol S/0.08 mmol NMBB= 3.91) than those used in the present work (0.094 mmol sulfur/0.78 mmol NMBB =0.12 corresponding to 1.2 wt% sulfur added; 0.27 mmol sulfur/0.78 mmol NMBB=0.34 corresponding to 3.4 wt% sulfur added).

Addition of 3.4 wt% sulfur provides 82.5% conversion, the highest observed in any of the tests reported in this paper. Naphthalene is the major product. In other reactions, the mol% of naphthalene and 4-methylbibenzyl are roughly comparable, as would be

expected from formation of these two compounds via scission of bond **a**. Reaction in the SFIO + sulfur system, which gives almost the same level of conversion (78.2%) provides a good example of this, where naphthalene and 4-methylbibenzyl are 64.1 and 59.6 mol%, respectively. However, in the reaction with 3.4 wt% added sulfur, the similar concentrations of these two products no longer holds, with 74.4 mol% naphthalene but only 32.3 mol% 4-methylbibenzyl.

This discrepancy suggests that secondary reactions may be responsible for the observed product distribution. Two alternatives can be considered: Scission at bond **a** followed by demethylation of the 4-methylbibenzyl would leave naphthalene as one major product, and a mixture of 4-methylbibenzyl and bibenzyl as other major products. Scission at bond **b** would produce bibenzyl and 1-methylnaphthalene; a subsequent demethylation of the 1-methylnaphthalene would form the observed naphthalene. Indeed, the methyl group in 1-methylnaphthalene is somewhat labile, as indicated by the facile isomerization to 2-methylnaphthalene, a product observed only at high levels of conversion. However, the reaction pathway $\text{NMBB} \rightarrow \text{bibenzyl} + 1\text{-methylnaphthalene} \rightarrow \text{naphthalene}$ could not easily account for the formation of significant amounts of 4-methylbibenzyl, which is indeed observed among the products, at 32.3 mol%. It would be necessary to invoke a transalkylation reaction of 1-methylnaphthalene and bibenzyl that would be selective for monomethylation at the 4-position of bibenzyl. It seems that the first alternative, $\text{NMBB} \rightarrow \text{naphthalene} + 4\text{-methylbibenzyl} \rightarrow \text{bibenzyl}$, is the more likely.

It should be noted that, unlike in other reaction systems, cleavage of both bond **a** and bond **b** is equally important in the reaction with 3.4 wt% sulfur. Two of the resulting products seem to undergo significant secondary reactions, as shown in Scheme I. (In other words, sulfur-induced bond cleavage of $\text{C}_{\text{ar}}\text{--C}_{\text{al}}$ is not as selective as cleavage induced by the iron sulfide catalysts.) Some of the naphthalene may be formed from 1-methylnaphthalene, and some of the bibenzyl may be from 4-methylbibenzyl. At present we do not have enough evidence to specify quantitatively the contribution from the two secondary demethylation reactions.

Scheme I.

Reactions in Sulfided Reactors. When conducting the reactions with added sulfur, we observed that sulfur appears to have a permanent effect on the stainless steel reactor walls, as can be from Table 5.2, Figures 5.4 and 5.5. Even new reactors turn black inside after reaction with sulfur, depending on the sulfur concentration. We did not conduct a detailed study of the sulfidation process itself, nor an analysis of the products. A useful review of sulfidation of stainless steels (and other alloys) is available.⁴⁴ Sulfidation can be a problem in refinery vessels.⁴⁵ Sulfur vapor readily attacks stainless steels above 444°C.⁴⁶ In some cases, an outer layer of the corrosion deposit has a composition Fe_{1-x}S , similar to that of pyrrhotite.⁴⁴ The catalytic properties of reactor walls in coal tar processing has been known for some time.^{25,47}

Although it is reported that sulfide scales are not as adherent to stainless steels as are oxide scales,⁴⁶ in our experiments the black sulfide layer could not be removed mechanically from the reactor walls. The black layer was not removed by treatment with potassium hydroxide in aqueous isopropanol for up to three days. Conversion of NMBB in a sulfided reactor was 23.0 wt% (Table 5.2), comparable to the 23.9 wt% observed with iron(II) sulfate + sulfur. Once again the major products resulted from scission of bond **a**, being naphthalene and 4-methylbibenzyl. For comparison, the non-catalytic reaction in a new reactor showed a conversion of 3.9 wt%, with cleavage at both bonds **a** and **c** being important. This apparent wall effect could be reduced by immersing a sulfided reactor in 6N hydrochloric acid for 5 min. Conversion was halved, to 11.6 wt% (Table 2) with no effect on the principal reaction pathway.

Figure 5.4. Illustration of wall effects on reactions of NMBB at 400°C.

Figure 5.5. The effect of a sulfided reactor on NMBB conversion is similar to that which would be obtained by addition of 1 wt% sulfur.

We postulate that longer treatment in HCl would completely remove the catalytic sulfide scale and once more provide "non-catalytic" conversions of $\approx 5\%$. However, because of the well-known susceptibility of stainless steels to stress corrosion cracking in chloride environments,⁴⁶ we did not wish to compromise the mechanical integrity of the reactors and did not conduct a more severe reaction in HCl.

To test whether the apparent catalytic effect of sulfided reactor walls was indeed an effect of the walls, or was an artifact of elemental sulfur trapped in the reactor, we washed sulfided reactors with chloroform and ethanol to remove any material trapped in the upper stem of the reactors. Experiments performed after this treatment showed no difference

compared to reactions done without washing the reactor. The wall effect does indeed seem to be due to the formation of a sulfide layer on the reactor walls.

Summary and Conclusions

A variety of iron compounds catalyze the hydrogenolysis of NMBB. For most, but not all, of these compounds, the conversion is significantly enhanced by the addition of sulfur to the reactor. In fact, the conversion of NMBB can also be enhanced by the addition of sulfur itself, even in the absence of any additional iron compound. The conversions observed in "sulfur only" reactions depend on the specific level of sulfur addition used. Sulfiding the reactor walls also serves to enhance conversion; the effect of the sulfide layer on the walls can be reduced by treatment in 6*N* hydrochloric acid. We presume that a sufficiently vigorous acid attack could eventually destroy the catalytic effect of the sulfided walls completely, and remove any wall effect.

All of the reactions result in the production of naphthalene and 4-methylbibenzyl as the major products. These compounds arise from cleavage of NMBB at bond *a*. Hydrogenation of NMBB itself or of the primary reaction products is a minor process under our reaction conditions (400°C, 6.9 MPa H₂ cold, 30 min.). The addition of 3.4 wt% sulfur enhances a second reaction pathway, leading to bibenzyl and methylnaphthalene via bond *b*.

Ferrocene behaved differently than superfine iron oxide or iron(II) sulfate, in that conversions in ferrocene + sulfur reactions actually dropped relative to reactions without sulfur. We have not yet determined the reason for this behavior, but find that it is consistent with other systems in which sulfur is added with cyclopentadienyl-containing catalyst precursors.^{41,42}

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- 40 An anonymous reviewer has kindly provided the published information that their group and others have seen 4-(2-naphthylmethyl)biphenyl, up to 4% of the original 4-(1-naphthylmethyl)biphenyl. We do not know whether these two NMBB isomers co-elute on the GC column used in this work, but we analyzed one batch of the NMBB samples purchased from TCI America and found only one NMBB peak by GC-MS and GC. We can not rule out the possibility that 4-(2-naphthylmethyl)biphenyl may be formed from isomerization of 4-(1-naphthylmethyl)biphenyl under the reaction conditions.
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Chapter 6.

Hydrocracking of 4-(1-Naphthylmethyl)bibenzyl Using Organometallic Fe Catalyst Precursors with and without Sulfur

Introduction

A detailed literature review on previous studies on iron-based catalysts has been presented in Chapter 5. Various iron containing catalysts have been investigated for their use in hydroliquefaction of coal ever since Bergius (1) demonstrated the feasibility of the process. Conventional iron catalysts (2,3) have been widely used either unsupported or as catalysts dispersed directly onto coal. Iron catalysts have generally a lower cost and lower environmental detriment than Mo, Ni and Co catalyst precursors. The search for active high surface area iron particles has become recently an important part in the development of a cost effective direct coal liquefaction process (4,5).

To examine what determines the activity and selectivity of Fe catalysts for hydrogenation and hydrocracking, various molecular precursors with Fe in different chemical environments have been tested in this work to help understand the influence of precursor structure and the effect of sulfur addition on the activity and selectivity of resulting Fe catalysts in model reactions of 4-(naphthylmethyl)bibenzyl (NMBB). We have examined various precursors, including a thiocubane type cluster $\text{Cp}_4\text{Fe}_4\text{S}_4$, a cyclopentadienyliron dicarbonyl dimer $\text{Cp}_2\text{Fe}_2(\text{CO})_4$, ferrocene Cp_2Fe , a series of carbonyl precursors including $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, and $\text{Fe}_3(\text{CO})_{12}$, and superfine iron oxide with average particle size of 30 Å (SFIO).

This chapter describes the screening of a series of selected iron carbonyl complexes and other iron compounds as precursors of dispersed catalysts for hydrocracking of 4-(1-Naphthylmethyl)bibenzyl, NMBB.

Experimental Section

Preparation of Catalyst Precursors. The complex $\text{Cp}_4\text{Fe}_4\text{S}_4$ (Fe4) was prepared according to the method described in the literature, based on the procedure of Schunn, Fritchie and Prewitt as described in Chapter 4. The thiocubane cluster and all other organometallic compounds were stored at - 25 °C prior to use. Recrystallization of the iron cluster was carried out quickly. The crystalline material is stable on exposure to air but decomposes slowly in solution.

$\text{Fe}(\text{CO})_5$, $\text{Cp}_2\text{Fe}_2(\text{CO})_4$, $\text{Fe}_2(\text{CO})_9$, $\text{Fe}_3(\text{CO})_{12}$ and elemental sulfur, were purchased from Aldrich, the model compound NMBB from TCI America. GC-MS confirmed sufficient purity of NMBB (> 99 %) and it was used without further purification. The superfine $\alpha\text{-Fe}_2\text{O}_3$ (hematite) was obtained as a brown, free flowing powder with a surface area of $250.5 \text{ m}^2/\text{g}$ and a bulk density of 0.05 g/ml from Mach I Inc., 340 East Church Road, King of Prussia, PA 19406. It is available under the trade name "NANOCAT (R) superfine Iron Oxide (SFIO)".

An additional bimetallic sample, $\text{CuZr}_2\text{P}_3\text{O}_{12}$ was also tested as catalyst in this work. $\text{CuZr}_2\text{P}_3\text{O}_{12}$ was prepared by Dr. Lynch and Dr. Brown of Pennsylvania State University. The sample is a green/grey dry powder that shows no thermal expansion even at high temperature and should keep its pore structure.

Model compound reactions. A stainless steel reactor (tubing bomb) with a capacity of 33 ml was loaded with ca. 0.25 g NMBB, 2.11 wt % catalyst precursor and 0.125 g solvent (tridecane; molar ratio NMBB/tridecane 1:1). The reactor was purged three times with H_2 and then pressurized with 6.9 MPa H_2 at room temperature for all experiments. A preheated fluidized sand bath was used as heating source and the reactor agitated via an oscillator by vertical shaking of the horizontal micro reactor (about 240 strokes/min.) After the reaction the hot tubing bomb was quenched in cold water and the gaseous products collected in a gas bag for further analysis. The internal standard dodecane was added into the reactor after the reaction, and then the contents were washed with about 15 ml CH_2Cl_2 and filtered. The liquid contents were washed with 15 ml CH_2Cl_2 through a low speed filter paper and stored in small glass bottles for qualitative and quantitative GC analysis. All runs were carried out at least twice to confirm reproducibility.

The compounds were identified by capillary gas chromatography-mass spectrometry (GC-MS) using a Hewlett-Packard 5890 II GC coupled with a HP 5971A mass-selective detector operating at electron impact mode (EI, 70 eV). The column used for GC-MS was a J&W DB-17 column; 30-m X 0.25-mm, coated with 50 % phenyl - 50 % methyl polysiloxane with a coating film thickness of $0.25 \text{ }\mu\text{m}$. For quantification a Perkin Elmer 8500 capillary GC with a flame ionization detector and the same type of column (DB-17) was used. Both Perkin Elmer 8500 GC and GC-MS were programmed from 40 to $280 \text{ }^\circ\text{C}$ at a heating rate of $4 \text{ }^\circ\text{C}/\text{min}$ after a 5 min isothermal holding at $40 \text{ }^\circ\text{C}$ and a final time of 20 min. The response factors of 10 pure compounds were determined.

Results and Discussion

Catalyst Precursor Features. Little work has been done on comparison of catalytic effects between mixed metal carbonyls, inorganic- and organometallic heteroatomic precursors. The organometallic complex iron pentacarbonyl (Scheme I) is a yellow, flammable liquid with a boiling point of 103 °C. This substance is highly toxic and forms explosive mixtures with air. $\text{Fe}(\text{CO})_5$ is a 18 VE (valence electron) complex with krypton electron configuration. Iron pentacarbonyl consists of a trigonal bipyramidal structure. The axial Fe-C- bonds are longer than the equatorial bonds. The complex decomposes above 150 °C into its components Fe and carbon monoxide.

Scheme I: Structures of iron carbonyls (top) and cyclopentadienyliron dicarbonyl dimer: $\text{Cp}_2\text{Fe}_2(\text{CO})_4$.

The cluster compound (scheme 1) $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ (mp 194 °C, dec.) consists of two iron atoms with capping cyclopentadienyl units, two bridging and two terminal carbon monoxide units. The metal-metal distance is 249 pm. $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ is a molecule with fluctuating structure in

solution. IR and NMR spectroscopy show a redistributing of terminal and bridging CO-moieties. The intermediate states show Cp-units changing from trans to cis position. The metal-metal bond is not involved in this process. Scheme I also compares the structures of the three iron carbonyl compounds.

Scheme 2: Structure of the thiocubane cluster $\text{Cp}_2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_4$.

The preparation and structural properties of $[\text{C}_5\text{H}_5\text{FeS}_4]$ (Scheme II) are described in Chapter 4. The thiocubane-type complex consists of an elongated tetrahedron of iron atoms with a sulfur atom over each face and a cyclopentadienyl group projecting from each corner. The overall symmetry of the molecule is D_{2d} . The interiron bonds have a length of 2.618 Å and 2.644 Å. The different bond lengths are possibly due to crystalline forces caused by different hybrid character of the orbitals used in forming the interiron bond. The average iron-iron bond is greater than those found in the carbon-bridged complexes, but lies in the center of the range found for sulfur-bridged Fe-Fe bonds. The long edges of the iron tetrahedron are 3.368 Å in length and are not interiron bonds. There are two classes of Fe-S bonds realized, those paralleling the long axis of the tetrahedron averaging 2.256 Å in length and those bridging the interiron bonds averaging 2.206 Å. The average Fe-Cp distance of 1.757 Å is somewhat longer than the value found in ferrocene, but agrees very well that of 1.75 Å found in $[(\text{Cp})\text{Fe}(\text{CO})_2]_2$. Other tetrahedral complexes are known and also based on transition-metal ligand cubic structures.

The α -form of superfine iron oxide from Mach 1 occurs naturally, unlike its γ -analogue. The structure is made in the α -form by distribution of Fe^{3+} -ions into $2/3$ of all octahedral O^{2-} -notches.

Analysis of Fe Catalysts. Catalyst samples for BET and XRD analysis were prepared in similar reactors from ca. 1 g precursor and 4 g tridecane at 400 °C under 6.9 MPa H_2 pressure for 30 min. XRD data were obtained from a Scintag I (Scientific Computer and Instruments, USA). Surface area measurements were conducted using a Quantachrome Autosorb I Gas Sorption system.

Hydrocracking of NMBB

The initial stage of a catalytic reaction involves catalyst activation at elevated temperatures, depending on the type of catalyst precursor. It is known (7-9) that some precursors like metal carbonyls require the addition of sulfur for sufficient activity. There seems (10) to be consensus that the sulfides of the transition metals are more active in catalytic hydroliquefaction than their oxides. The scientific reason for this remains unclear. The activation reaction is difficult to perform and iron carbonyls tend to form less reactive iron carbides and oxides (11) during the activation process.

The present results in Tables 6.1 and 6.2 revealed several interesting trends. Even the catalysts without sulfur can display certain activity. The particles from $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ showed the highest activity among all the precursors examined in the absence of added sulfur. Scheme III to VIII show the products identified from reactions using different Fe carbonyl precursors with and without added sulfur. The activity of catalysts from Fe carbonyls decreased with increasing number of irons in the carbonyl compounds: $\text{Fe}(\text{CO})_5 > \text{Fe}_2(\text{CO})_9 > \text{Fe}_3(\text{CO})_{12}$; adding sulfur increased their activity but their activities rank the same both with and without sulfur addition.

Surprisingly, $\text{Cp}_4\text{Fe}_4\text{S}_4$ exhibited the lowest activity, although it has the S-to-Fe ratio closest to pyrrhotite (Fe_{1-x}S , where $x = 0$ to 0.12) which is thought to be the active phase. The nano-scale SFIO particles performed at an activity level similar to that of $\text{Fe}_2(\text{CO})_9$ in the absence of sulfur, but afforded the highest NMBB conversion when S was added. Ferrocene is more effective in hydrocracking reactions of NMBB than the inorganic iron complex $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Table 6.2). Sulfur added to iron sulfate had the expected beneficial effect on NMBB conversion. But sulfur added to ferrocene decreased the activity of resulting catalyst. The other iron containing organometallic complex that showed a similar trend in conversion after sulfur addition was

$\text{Cp}_2\text{Fe}_2(\text{CO})_4$. Both complexes have cyclopentadienyl ligands as common features. Another precursor with Cp-functionalities and sulfur in the precursor molecule ($\text{Cp}_4\text{Fe}_4\text{S}_4$) showed very low activity too. There is apparently a negative correlation between the conversion of iron containing complexes and the presence of cyclopentadienyl/sulfur units.

Table 6.1. Effect of Fe containing catalyst precursors on NMBB hydrocracking at 400 °C.

Catalyst Precursors	$\text{Cp}_2\text{Fe}_2(\text{CO})_4$	$\text{Fe}(\text{CO})_5$	$\text{Fe}_2(\text{CO})_9$	$\text{Fe}_3(\text{CO})_{12}$	$\text{Fe}(\text{CO})_5$ + S	$\text{Fe}_2(\text{CO})_9$ + S	$\text{Fe}_3(\text{CO})_{12}$ + S	$\text{Cp}_2\text{Fe}_2(\text{CO})_4$ +S
Conv, wt %	62.2	45.6	24.7	22.1	61.2	51.5	45.7	21.3
Prod, mol %								
Benzene	0.6				1.3		0.7	0.9
Toluene	1.6	1.3	0.8	1.5	2.3	2.3	1.9	
p-Xylene	0.5	0.2	0.2	0.3	0.8	0.4	0.7	0.2
Tetralin	8.5	4.2	2.2	2.0	2.6	1.5	2.0	0.3
Naphthalene	38.1	42.8	20.3	23.3	67.8	47.8	46.6	20.4
2-MTHN ^a								
1-MTHN	0.8	0.3	0.4					
2-MN ^b	0.2				1.3	1.1	0.8	0.1
1-MN	2.5	2.6	1.0	1.6	5.3	3.7	3.4	1.1
BB ^c	4.0	3.6	1.6	1.8	7.6	6.7	5.5	1.5
Benzyl-naphthlene	0.3	0.1						0.2
4-MBB ^d	40.1	35.7	20.3	16.2	52.7	41.1	33.6	18.5
TH-NMBB ^e	14.4	0.8	1.4					0.3

^aMethyltetrahydronaphthalene; ^bmethylnaphthalene; ^cbibenzyl; ^dmethylbibenzyl; ^etetrahydro-NMBB.

Scheme III

Scheme IV

Scheme V

Model compound: NMBB
 Catalyst: $\text{Fe}_2(\text{CO})_9$
 Metal concentration: 2.11 wt % Fe
 Solvent: Tridecane
 Internal Standard: Dodecane
 Reaction time: 30 min
 Reaction temperature: 400 °C
 Pressure: 6.9 MPa H₂
 Stroking rate: 246/min

Scheme VI

Model compound:

Catalyst:

Metal concentration:

Sulfur concentration:

Solvent:

Internal Standard:

Reaction time:

Reaction temperature:

Pressure:

Stroking rate:

NMBB

 $\text{Fe}_2(\text{CO})_9$

2.11 Wt % Fe

1.2 wt % S

Tridecane

Dodecane

30 min

400 °C

6.9 MPa H_2

246/min

Scheme VIII

Table 6.2. Effect of Fe precursors with different ligands on NMBB hydrocracking at 400 °C.

Catalyst Precursors	Non-catalytic	Superfine Fe ₂ O ₃	Superfine Fe ₂ O ₃ + S	FeSO ₄ x 7 H ₂ O	FeSO ₄ x 7 H ₂ O + S	Cp ₂ Fe	Cp ₂ Fe + S	Cp ₄ Fe ₄ S ₄
Conv, wt %	3.9	27.1	78.2	3.7	23.9	15.8	9.6	11.7
Prod, mol %								
Benzene	0.6	0.2	0.5					2.5
Toluene	0.3	1.3	1.9		1.3	1.6	1.1	
p-Xylene		0.3	0.7					
Tetralin	0.2	3.0	4.0		0.6	0.4	0.3	
Naphthalene	0.6	16.4	64.1	4.5	24.0	13.8	10.3	10.9
2-MTHN ^a			0.2					
1-MTHN		0.5	0.4					
2-MN ^b			1.4					
1-MN			5.8		1.5	5.6	0.5	0.1
BB ^c		1.0	8.9	0.6	2.5	2.6	0.6	0.4
Benzyl naphthalene	0.9							
4-MBB ^d	1.3	17.4	59.6	2.6	19.1	9.4	7.4	10.8
TH-NMBB ^e		7.3	5.5					

^aMethyltetrahydronaphthalene; ^bmethylnaphthalene; ^cbibenzyl; ^dmethylbibenzyl; ^etetrahydro-NMBB.

To better understand the relationship between catalyst composition and catalytic activity, surface area and XRD measurements were carried out. The surface area of freshly generated catalyst particles was measured and the phase identified through X-ray diffraction. Our investigation of in situ generated iron catalyst from organometallic precursor revealed higher surface areas for pyrrhotite than magnetite particles. From XRD-measurement, it was found that iron carbonyl was transformed at 400 °C into magnetite Fe₃O₄. Sulfur added to Fe(CO)₅ yields pyrrhotite as black material. Generally iron sulfides have higher surface areas than magnetite. The effect of sulfur addition to iron carbonyls on the surface area is illustrated in Table 6.3.

Table 6.3. BET Surface area and phase of activated catalysts.

Precursor Molecule	BET m ² /g	Meso Pore m ² /g	Phase Identified from XRD
Fe(CO) ₅	3.22	3.22	Fe ₃ O ₄
Fe ₂ (CO) ₉	7.73	7.73	Fe ₃ O ₄
Fe ₃ (CO) ₁₂	17.6	17.6	Fe ₃ O ₄
Fe(CO) ₅ + S	1.56	1.54	FeS
Fe ₂ (CO) ₉ + S	3.58	3.45	FeS
Fe ₃ (CO) ₁₂ + S	2.93	2.93	FeS
Ferrocene + S	21.7	20.5	FeS
Cp ₄ Fe ₄ S ₄	11.39	9.33	FeS
Fe ₂ O ₃	228	228	---

Surprisingly, higher surface areas can be generated from higher iron carbonyl clusters. The BET surface area increases dramatically with increasing number of inter iron bonds. A similar trend can be observed when sulfur is added to the corresponding iron carbonyls. However, pyrrhotite coming from Fe carbonyls has a substantially lower surface area than the analogue generated from ferrocene and sulfur. Even the sparingly soluble Cp₄Fe₄S₄ yields after thermal activation higher surface area material than most iron carbonyls which are more soluble in hydrocarbons and are expected to lead to higher dispersion. The XRD-pattern reveals pyrrhotite as main product. This excludes iron carbide as the activity inhibiting material. However, the microstructure can be influenced by minute traces of impurities. Further elemental analysis will help clarify this issue.

Catalytic Performance of CuZr₂P₃O₁₂. We also tested a copper zirconium phosphate CuZr₂P₃O₁₂, a material with stable pore structure, even at elevated temperatures. The results are given in Table 6.4. Hydrocracking experiments using the copper zirconium phosphate at 400 °C gave no more conversion than a non-catalytic run. The beneficial effect of sulfur addition

Table 6.4. Effect of $\text{CuZr}_2\text{P}_3\text{O}_{12}$ and Sulfur addition on hydrocracking reactions of NMBB at 400 °C

Catalyst Precursors	$\text{CuZr}_2\text{P}_3\text{O}_{12}$	$\text{CuZr}_2\text{P}_3\text{O}_{12}$ + S	Sulfur 3.4 wt %	Sulfur 1.2 wt %	None [sulfided reactor]	None [reactor HCl treated]
Products [mmol %]						
Benzene						
Toluene	1.2	2.6	4.9	1.4	1.0	1.0
p-Xylene						
Tetralin	0.6	3.0	2.9	0.8	0.8	0.4
Naphthalene	13.8	50.3	74.4	24.8	19.1	10.8
2-MTHN			0.4			
1-MTHN						
2-Methylnaphthalene		0.6	7.8			
1-Methylnaphthalene	0.8	4.0	9.5	1.7	0.8	0.7
Bibenzyl	2.1	7.2	42.5	2.4	1.0	1.2
Benzyl-naphthalene ^b						
4-Methylbibenzyl	10.3	43.2	32.3	22.1	18.3	9.7
TH-NMBB- derivatives						
Conversion [wt %]	13.3	54.4	82.5	26.1	23.0	11.6

^a Reactor residence time in preheated sand bath: 30 min. ^b Also called naphthyl phenyl methane.

could once more be demonstrated in another experiment. Sulfur added to $\text{CuZr}_2\text{P}_3\text{O}_{12}$ led to an increase in conversion of about 50 %. The very low activity of the sulfur free copper zirconium phosphate stimulated our interest to study the influence of sulfur on hydrocracking reactions. A series of experiments was carried out to determine the impact of sulfur concentration on NMBB conversion. It was found that increasing sulfur concentration (starting at 1.2 wt %) led to increasing model compound conversion.

Distribution of products from NMBB

Hydrocracking of NMBB yields three product categories that can be explained by the cleavage of the bonds between the aromatic moieties. Those coming from hydrocracking reactions form the major pool of reaction products, followed by hydrogenation and isomerization products. As can be seen from Tables 1 and 2, all iron containing catalyst precursors give a similar ratio of main products. It is apparent that ferrous catalysts cleave NMBB preferably in position α . Increasing conversion leads in most experiments to a proportional increase in the ratio of major products. The following compounds can be found as main products: naphthalene, 4-MBB, bibenzyl and tetralin.

Mechanistic Considerations

The structure of NMBB influences the cleavage pathway. Catalyst particles act as hydrogen transfer agents and stabilize the intermediate radical. They prevent undesirable recombination of the free radicals to polymeric material. Naphthalene and 4-methylbibenzyl are formed predominately in catalyzed reactions, indicating that bond α in NMBB is the most reactive unit in the Fe-catalyzed runs. However, different ligand environment and oxidation state of the precursor molecule can reverse the observed preference for bond α cleavage (e.g. MoCl_3). Farcasiu et al. (12-14) suggested a reaction mechanism in which the first stage consists of the formation of a radical cation. The loss of electron density leads to a weakened α -bond which can then be broken relatively easily. This is in contrast to model studies in which phenyl-containing compounds undergo preferably β -cleavage (15). In the work of Penn and Wang (15) radical cations were generated in the mass spectrometer under a variety of conditions which had little impact on the bond cleavage pathway. Preference for β -cleavage was explained by resonance stabilization of the intermediates. Both intermediates are resonance stabilized. Thermochemical calculations (16) show that reaction pathway β is 30 kcal/mol lower for both neutral and radical cationic species than pathway α . In contrast, neither of the intermediates resulting from bond α cleavage is stabilized. However, in the presence of a catalyst, the major reaction pathway mainly involves the cleavage of bond α . Related work (17) investigated the reaction mechanism of bond scission of naphthyl-

derivatives and proposed the addition of a hydrogen radical to the ipso position of the naphthyl-unit to generate a relatively stable benzylic radical. Our data, as shown in Tables 1 and 2 support the hypothesis that all iron containing catalyst precursors induce preferably the scission of bond α in NMBB. It is believed (18) that strong hydrogenation catalysts show higher selectivity towards α cleavage than less active iron catalysts. High catalytic activity is accompanied by rich hydrogen supply adsorbed on the catalyst surface. Model compounds with aromatic ipso positions are prone to subsequent reactions with single hydrogen atoms, leading to hydrogenation products. The less active iron catalysts are not capable of multiple hydrogen transfer during the short contact time between NMBB and model compound. Thus cleavage of NMBB occurs with higher selectivity. The structure of the catalyst precursors and the sulfur addition affect the reactions on the surface of in situ generated catalysts.

Summary and Conclusions

We have examined a cyclopentadienyliron dicarbonyl dimer $\text{Cp}_2\text{Fe}_2(\text{CO})_4$, a thiocubane type cluster $\text{Cp}_4\text{Fe}_4\text{S}_4$, a series of carbonyl precursors including $\text{Fe}(\text{CO})_5$, $\text{Fe}_2(\text{CO})_9$, and $\text{Fe}_3(\text{CO})_{12}$, and superfine iron oxide with average particle size of 30 Å (SFIO). The results with the above precursors revealed several interesting trends.

First, even the catalysts without sulfur can display certain activity. Some iron containing catalysts from certain iron carbonyls have higher activity in the sulfur-free form, contrary to conventional wisdom. The particles from $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ showed the highest activity among all the precursors examined. The activity of catalysts from Fe carbonyls decreased with increasing number of irons in the carbonyl compounds: $\text{Fe}(\text{CO})_5 > \text{Fe}_2(\text{CO})_9 > \text{Fe}_3(\text{CO})_{12}$.

Adding sulfur to Fe precursors with Cp-ligands decreased the activity of the resulting catalyst. This is in distinct contrast to the cases with iron pentacarbonyl and superfine Fe_2O_3 , where S addition increased their catalytic activity substantially. A positive correlation between sulfur addition and increased activity can be seen, but a reversed trend between Fe cluster size and hydrocracking conversion could be observed, for carbonyl-type Fe precursors. It is apparent that the activity and selectivity of Fe catalysts for NMBB conversion depends strongly on both the type of ligand environment, the oxidation state and the number of intermetal bonds in the molecular precursor.

Another interesting trend is that the activity levels of catalysts from Fe carbonyls rank the same both with and without the S addition. With one exception, adding sulfur to all the

reactions increased NMBB conversion, but decreased yields of hydrogenation products.

We subsequently examined a S-containing precursor, $\text{Cp}_4\text{Fe}_4\text{S}_4$. Surprisingly, it exhibited the lowest activity, although it has a S-to-Fe ratio closest to pyrrhotite (Fe_{1-x}S , where $X= 0$ to 0.12) which is thought to be the active phase. However, the selectivity for the α -cleavage of the C-C bond in NMBB is the highest with $\text{Cp}_4\text{Fe}_4\text{S}_4$. The nano-scale SFIO particles performed at an activity level similar to that of $\text{Fe}_2(\text{CO})_9$ in the absence of sulfur, but afforded the highest NMBB conversion when S was added.

Based on the product distribution, we can define two main reaction pathways for NMBB over Fe catalysts: one is α -cleavage (path I) and the other is hydrogenation to form THNMBB (path II). Probably these two pathways start from the same intermediate, the radical formed after hydrogen atom attack on ipso position on naphthalene ring. The path I is favored by β -cleavage of the radical intermediate, but path II is favored when the radical intermediate abstracts another hydrogen. They compete with each other. The structure of catalyst precursors and the sulfur addition affect the reaction pathways on the surface of in situ generated catalysts, and such information can be used to guide further research on the catalysis.

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Chapter 7

Hydrodesulfurization of Dibenzothiophene 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, $(\text{NH}_4)_2\text{MoS}_4$, 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 $\text{Cp}_2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_4$ (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 form 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 7.1. 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 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 $\text{Mo(CO)}_6 + \text{S}$. The ratio of cyclohexylbenzene to biphenyl is 0.48 for the ATTM reaction and 0.46 for $\text{Mo(CO)}_6 + \text{S}$.

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 $\text{Mo(CO)}_6+\text{S}$ 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 7.2. There are some unidentified products which are not reported in Table 7.2. 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 7.1. 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 solvent.

Figure 7.1. 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 7.2, 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 7.2.

We also investigated molybdenum(III) chloride as a catalyst precursor at the 36 mol% loading. Results are provided in Table 7.3. 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 ATT_M 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 MoCl₃ 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 MoCl₃+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 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/Al₂O₃ catalyst²³ and a Mo(CO)₆/SiO₂-Al₂O₃ 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 7.2 (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_9S_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 $\text{Cp}_2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_4$, whose structure is given in Scheme II.

Scheme 2. Structure of the thiocubane cluster $\text{Cp}_2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_4$.

The results with this bimetallic thiocubane (MoCo-TC2) are shown in Table 7.3. 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

Table 7.1. Conversions and product yields from catalytic hydrodesulfurization of dibenzothiophene with molybdenum-based precursors at 0.5 and 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: ^atridecane, ^boctadecane. ^cConversion is based on the yields of recovered products. ^dProducts: biphenyl (BP), tetrahydrodibenzothiophene (TH-DBT), cyclohexylbenzene (CHB), bicyclohexyl (BCH), and benzene (BNZ). HDS product = sum of yields of BP, CHB, BCH, and BNZ.

Table 7.2. Conversions and product yields from catalytic hydrodesulfurization of dibenzothiophene with molybdenum-based precursors at 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: ^atridecane, ^boctadecane, ^cheptadecane.

Table 7.3. Conversions and product yields from catalytic hydrodesulfurization of dibenzothiophene with various molybdenum-, iron-, and cobalt-containing precursors, at 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: ^atridecane, ^boctadecane.

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, cobalt³⁰) 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 7.3. 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 stoichiometry. Earlier work³³ 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, $\text{Co}_2(\text{CO})_8$, $\text{Fe}(\text{CO})_5$, and $\text{Cp}_2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_4$, 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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Chapter 8

Hydrodeoxygenation In Coal Liquefaction Systems Using Novel Organometallic Catalyst Precursors

Introduction

The present concensus is that direct coal liquefaction will be a catalytic process. High conversions (>88%) have been achieved using "conventional" liquefaction catalysts of iron and molybdenum[1]. As we can achieve good conversions with regular catalysts, the main reason for considering "unconventional" catalysts must be to improve the product quality. A major concern with product quality is the abundant oxygen content. Phenols can comprise as much as ~40% of the liquefaction distillates in low-rank coals[2].

Oxygen-containing functional groups are present in virtually all coals [3]. Ethers have been proposed as sites for depolymerization [4], and together with carboxyls and phenolics, have been implicated in facilitating repolymerization reactions [5, 6]. Phenols have been identified as components of coal-derived distillates [2, 7], and oxygenated compounds have been connected to the instability of these distillates [8].

Low-rank coals include significantly more oxygen-containing groups than coals of higher rank [9, 10]. With the increase in the extraction of low-rank coals in the U.S. and research into their use as liquefaction feedstocks [5, 11, 12], the ability to remove oxygen functional groups becomes even more important. Compounds containing these functional groups are usually removed down-stream in a catalytic hydrodeoxygenation step. Supported CoMo and NiMo catalysts facilitate oxygen removal in these processes [8, 13, 14]. However, the use of these catalysts increases complexity and cost of the process. An alternative is to extract the phenols from the distillates, but this would discard ~40% of the potential product [2]. Therefore, deoxygenation during the liquefaction process itself would be beneficial. Utilization of either a CoMo, or a NiMo,

catalyst in a liquefaction stage has the potential to increase the quality of distillates, by combining hydrodeoxygenation and liquefaction in a single stage.

Sulfided metal catalysts have been considered desirable for liquefaction, because they are not readily poisoned by the heteroatom-containing compounds from the coal. Sulfided molybdenum catalysts are particularly active for liquefaction. Unfortunately, MoS_2 is insoluble in all common solvents, and is difficult to disperse onto the coal particles. A strategy to mitigate this problem is the use of catalyst precursors, soluble salts that presumably can be readily dispersed onto coal. The catalyst precursors may have little or no catalytic activity themselves, but decompose into an active form at the temperatures of the liquefaction reaction.

It would be neither easy nor efficient to obtain the promoting effect of nickel or cobalt by sequential dispersion of a molybdenum-containing catalyst precursor followed by application of a nickel or cobalt precursor. Instead, we hypothesized that this goal may be attainable with the use of bimetallic catalysts dispersed onto the coal using an appropriate precursor [15, 16].

Model compound studies were performed to investigate the capabilities of these catalyst precursors. The model compounds selected represent a variety of oxygen functionalities, possibly present in coals of differing ranks [17-19]. They include a carbonyl; an aryl-aryl ether; a heterocyclic ether; and a substituted phenol. The reactions of these compounds in the presence of several catalyst precursors under liquefaction conditions give an indication of the hydrodeoxygenating abilities of these precursors.

Liquefaction studies were then performed on a selection of coals of varying rank and oxygen content. Here we report an investigation of the effect a bimetallic organometallic precursor (CoMo-T2) on conversion and product distribution of these coals under liquefaction conditions. For comparison we have conducted the same reactions under non-catalytic conditions, and in the presence of ATTm, commonly used in liquefaction research.

Experimental

The model compounds studied were: anthrone, dinaphthyl ether (DNE), xanthene and 2,6-di-*t*-butyl-4-methyl phenol (DBMP). The coals studied were: DECS26 Wyodak (subB), November 21, 1997 DECS24 Illinois #6 (hvCb) and DECS23 Pittsburgh #8 (hvAb). These coals have oxygen contents (daf) of 16.92, 10.74 and 6.66, respectively.

All experiments were performed in 22 mL capacity microautoclave reactors made of stainless steel. A 0.5 g sample of the model compound, or a 4 g sample of coal (<60 mesh), was loaded into the reactor. 1-Methylnaphthalene was added as solvent in a 1:2 weight ratio to reactant, and catalyst precursors were added at 2.5 mol% for the model compound studies and 1 wt% concentration for coal. The catalyst precursors used were $(\text{NH}_4)_2\text{MoS}_4$ (ATTM), and $\text{Cp}_2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_4$, which for convenience we call CoMo-T2. (The symbol Cp represents the cyclopentadienyl group.) This precursor has a thiocubane structure, illustrated in Figure 1. Air was removed by flushing the reactor three times with H_2 to 7 MPa. The reactor was then repressurized to 7 MPa H_2 (cold). Reactions were performed at 400°C for 30 minutes in a fluidized sand bath. At the end of the reaction the reactor was quenched in cold water.

For the reactions with coal, the reactor contents were removed to a porous thimble. The liquid and solid products were separated by sequential Soxhlet extraction with hexane, toluene and THF for approximately 24 hours. The THF insoluble residues were washed with acetone, then with pentane to remove THF completely, and subsequently dried before weighing. Products from the model compound studies were extracted from the reactor with acetone.

Capillary gas chromatography (GC) and gas chromatography / mass spectrometry were used for the quantitative and qualitative analysis of the hexane solubles.

Results and Discussion

Model Compound Studies

Figures 8.2-8.5 show reaction schemes proposed as possible pathways to the product distributions observed. These schemes are derived from the analyses of reaction products. We have not determined kinetic constants for the various reactions, nor conducted detailed mechanistic studies. Therefore, while Figures 8.2-8.5 are consistent with the observation of the formation of various products, it should be recognized that other mechanisms may be possible. Tables 8.1-8.4 provide the product distributions for the respective model compounds under conditions of varying temperature and catalyst precursor. For the purposes of discussion, products have been grouped by the types of reaction involved in their formation, such as, for example, hydrogenation or deoxygenation. Figures 8.6-8.9 are plots illustrating the conversion of the starting materials into products grouped as reaction types. Generally, the addition of any catalyst precursor to a system, under the conditions studied, increases the total conversion to all products. For example, at 400°C dinaphthyl ether undergoes 26% conversion in non-catalytic reactions; this yield is increased to 72% in the presence of ATTM and 100% using CoMo-T2. However, any improvement in the product quality, which in these cases would be indicated by oxygen removal, ring hydrogenation, or both, in the presence of these precursors is also important. As discussed in the introduction, oxygen removal may occur by either of two major mechanisms: direct deoxygenation or oxygen removal after ring hydrogenation. The variation of all these factors, for the various oxygen functional groups and different catalysts, will be the main focus of the discussion that follows.

Figure 8.1. Structure of $\text{Cp}_2\text{Co}_2\text{Mo}_2(\text{CO})_2\text{S}_4$ (CoMo-T2).

Figure 8.2. Conceptual reaction scheme for the product distribution of anthrone.

Figure 8.3. Conceptual reaction scheme for the product distribution of dinaphthyl ether.

Figure 8.5. Conceptual reaction scheme for the product distribution of dibutylmethyl phenol.

Anthrone

For anthracene and related compounds hydrogenation and dehydrogenation reactions are most favourable at the 9- and 10-positions [20]. Therefore the most likely product of hydrogenation of anthrone is 9,10-dihydroanthracene (DHA).

Oxygen removal occurs readily for anthrone, even under non-catalytic conditions. Although the hydrogenation of anthrone in the absence of a catalyst is difficult, considerable oxygen removal is achieved through direct deoxygenation, forming anthracene. Hydrogenated products are only observed at higher temperatures and in low yields.

Hydrogenation reactions in general increase with temperature in most cases, but are enhanced considerably in the presence of a catalyst. Reaction at 350°C in the presence of the ATTM precursor is an exception to this trend, showing considerably more extensive hydrogenation than the reaction at 400°C. This particular experiment was performed at a later date with a new batch of ATTM to that used for previous reactions. In conjunction with other observations recently made in our laboratory, this result implies that ATTM undergoes severe changes in activity during aging. Therefore, the result obtained at 350°C is incomparable to the other results, and shall be excluded from the discussion. Studies in the effects of storage and aging on the activity of this catalyst precursor will be the subject of future work.

In the absence of a catalyst, the yield of anthracene is larger and no decrease from 350°C to 400°C is observed. This may be attributed to an equilibrium between anthracene and DHA, which favours the increased stability of the dehydrogenation product at higher temperatures, when the enhanced hydrogenation effect of a catalyst is not available.

Both precursors provide similar activities toward oxygen removal and ring hydrogenation, although the distribution of these hydrogenated products is quite different depending on the catalyst precursor used. CoMo-T2 appears to favour the formation of DHA, whereas use of ATTM results in greater yields of the products of more extensive

hydrogenation. At 400°C, for example, the yield of total hydrogenated anthracenes is 89.7% using ATTM and 89.6% with CoMo-T2. The difference is seen in that the yields of tetra- and octahydroanthracenes are much higher with ATTM. In this case, dihydroanthracene accounts for just under half of the total yield of hydrogenated anthracenes, while with CoMo-T2, dihydroanthracene makes up approximately three-quarters of the hydrogenated anthracenes.

Assuming an equilibrium between anthracene and DHA, all the oxygen-free products observed can be accounted for by the hydrogenation of anthracene and consequently are products of direct deoxygenation of anthrone. This explanation accounts for the lower yields of anthracene at 400°C in the presence of a catalyst, coinciding with increased yields of its hydrogenated products. Also, no hydrogenated products that still contain oxygen are observed, again suggesting that all hydrogenated products are formed from anthracene.

Further evidence of such a mechanism is provided by the percentage of oxygen-free products that are hydrogenated. At 350°C, hydrogenated compounds represent 73% of the total oxygen-free products from CoMo-T2. However, at 400°C, hydrogenated compounds represent 90% of the total oxygen-free products obtained with both catalysts. This suggests that oxygen removal is easier or faster, and hydrogenation then has to "catch up". If so, this would be quite consistent with the data from non-catalytic reactions that show oxygen removal by direct deoxygenation is fairly facile, but hydrogenation is not.

These results could also be achieved, however, if DHA is formed directly from anthrone by hydrogenation. In this case, the reduced anthracene yields would be attained by formation of 1,2,3,4-tetrahydroanthracene (THA) and its hydrogenation products, as well as by shifting the equilibrium reaction toward DHA formation. This would suggest that, in the presence of either ATTM or CoMo-T2, oxygen removal accompanied by hydrogenation would be favourable over direct deoxygenation. This may be a result of

the location of the carbonyl group at the 9-position, so that the product of the hydrogenative deoxygenation of anthrone would be the favoured 9,10-dihydroanthracene.

Both of these processes may occur at the same time, but in competition for the catalytic sites. If so, the product distributions imply that in the presence of CoMo-T2 hydrogenation is the dominant pathway for oxygen removal from anthrone (as shown by the higher yield of DHA), whereas in the presence of ATTM both mechanisms occur to similar extents (as indicated by roughly comparable yields of DHA and THA).

Both ATTM and CoMo-T2 have the capability to increase the conversion of carbonyls without phenol or naphthol production. This may be achieved by either rapid C=O cleavage prior to ring hydrogenation, rapid phenol conversion to oxygen-free products, or by the prevention of initial hydroxyl group formation or oxygen removal after initial ring hydrogenation. From the reactions of 2,6-di-*t*-butyl-4-methyl phenol (DBMP) with CoMo-T2, it can be seen that this precursor, although removing some hydroxyl functionality, does not promote the ready conversion of phenols to non-oxygen containing species. Therefore, it is likely that CoMo-T2 facilitates rapid carbonyl removal, either before or after ring hydrogenation.

2,2'-Dinaphthyl Ether

Dinaphthyl ether is substantially less reactive than anthrone with respect to both oxygen removal and ring hydrogenation. Again, hydrogenation reactions do not readily occur in the absence of a catalyst. However, in contrast to anthrone, hydrogenation can occur without prior oxygen removal. Naphthalene and 2-naphthol increase in yield as temperature increases in the absence of a catalyst precursor.

Hydrogenation products decrease as reaction temperature is increased from 350°C to 400°C under catalytic conditions. For ATTM all hydrogenation products decrease in yield from 350°C to 400°C, but in the presence of CoMo-T2, the reduction in the total yield of hydrogenation products is nevertheless accompanied by a slight increase in

tetralin yield. With both precursors, a substantial increase in naphthalene yield (by 12 percentage units in both cases) is observed at the higher reaction temperature.

If direct deoxygenation reactions increase at higher temperatures then the larger naphthalene yields suggest an enhancement of direct deoxygenation of dinaphthyl ether and 2-naphthol. In the absence of a catalyst, tetralin formation is negligible. Under catalytic conditions, the equilibrium between naphthalene and tetralin should favour hydrogenation under the temperatures studied. Also, the deoxygenation of dinaphthyl ether and 2-naphthol would be accompanied by the direct deoxygenation of any previously hydrogenated compounds (i.e. 5,6,7,8-tetrahydrodinaphthyl ether (THDNE) and 5,6,7,8,5',6',7',8'-octahydrodinaphthyl ether (OHDNE)), to form both naphthalene, tetralin, 2-naphthol and 5,6,7,8-tetrahydronaphthol (THnaphthol).

Naphthol yields diminish due to either hydrogenation to tetralin and THnaphthol or direct deoxygenation to naphthalene. In the presence of ATTM, decreases in naphthol yield are accompanied by increases in naphthalene yield, although clearly most of the naphthalene produced in these experiments derives from sources other than naphthol deoxygenation. In the presence of CoMo-T2, increases in tetralin and lower molecular weight products are observed when naphthol yields decrease. We noted above that tetralin was the only hydrogenated product of reactions with CoMo-T2 to increase in yield when temperature is increased from 350° to 400°C. The increase in tetralin yield, 4.4 percentage units, is very nearly accounted for by the corresponding reductions of yields of 2-naphthol and THnaphthol (which total 3.4 percentage units). These results suggest a difference in the process of oxygen removal depending on which catalyst precursor is used.

With regard to total conversion to all products, CoMo-T2 is considerably superior to ATTM at all temperatures. The yields of naphthalene for the two catalyst precursors are comparable at all temperatures, suggesting the differences in total conversion are due

to increased hydrogenation activity by CoMo-T2. Indeed, this is clearly shown by the substantially higher yields of tetralin from reactions with CoMo-T2.

Xanthene

Xanthene is very unreactive in our experiments. It does not react in the absence of a catalyst and undergoes little, or no, reaction at 300°C in the presence of a catalyst. Even under catalytic conditions at 400°C limited oxygen removal occurs. For both catalyst precursors, the products of direct deoxygenation increase with temperature. Products of oxygen removal by hydrogenation are only observed at higher temperatures (400°C), although C–O bond cleavage following ring hydrogenation is observed at 300°C.

At 350°C the products from reactions in the presence of both precursors are alkylphenols and cycloalkylbenzenes formed by C–O and C–C bond cleavage. However, at 400°C ATTM produces an increase in oxygen-free products with no increase in phenols, although conversion to non-oxygen containing species is low (12.3%).

Yields of oxygen-free products are observed with CoMo-T2 only at 400°C (14.1%), but with accompanying substantial increases in phenol formation. This gain in phenols may be attributed to the production of 1-methyl-2-phenoxybenzene, which reacts readily to form phenol, toluene and possibly 2-methylphenol.

For both precursors, the formation of C–C bond cleavage products (i.e. pentyl- and butylphenol) is a prominent reaction pathway at 350°C. However, at 400°C in the presence of ATTM the yields of these products decrease. An increase in those products formed through the cleavage of C–O bonds does occur. Reactions with CoMo-T2 also show an increase in C–O bond cleavage and direct deoxygenation products at 400°C, yet this increase is accompanied by a rise in C–C bond cleavage and hydrogenation products. Comparatively little ring hydrogenation occurs using either precursor, except at 400°C. For example, with ATTM, reaction products containing cyclohexyl or cyclopentyl rings comprise about a third of the total product yield at 350°C, but account for about two-

thirds of all products at 400°C. ATTM is superior to CoMo-T2 in providing deoxygenation of the products formed from xanthene conversion, though for both precursors oxygenated products dominate the product slate at all reaction temperatures.

2,6-Di-*t*-butyl-4-methylphenol

2,6-Di-*t*-butyl-4-methylphenol (DBMP) is highly reactive. Previous work from this laboratory has demonstrated a very rich thermally induced chemistry of highly alkylated phenols at 350°C and above [25,26]. Even under non-catalytic conditions, 100% conversion can be achieved (by *t*-butyl cleavage) at 400°C, although no reaction occurs at 300°C. Removal of the hydroxyl group is much more difficult to accomplish than is dealkylation, since no C–OH bond cleavage occurs in the absence of a catalyst. Ring hydrogenation also does not occur without a catalyst.

In the presence of either catalyst precursor, both hydrogenation and direct deoxygenation increase with temperature. The sequential removal of both *t*-butyl groups becomes more favourable under catalytic conditions, although aromatic C–OH cleavage appears to be substantially more facile than aromatic C–CH₃ cleavage. In fact, it is noteworthy that the methyl group survives virtually all reactions while debutylation occurs very easily even without a catalyst.

At 350°C using ATTM, almost all the starting material reacted and only a small portion remains as 2-*t*-butyl-4-methylphenol (BMP). The major product, 4-methylphenol, then undergoes catalytic hydrogenation and direct deoxygenation to form methylcyclohexane and toluene, respectively. At 400°C these reactions proceed to a greater extent, resulting in greater yields of both products. Methylcyclohexane can be produced by hydrogenation of toluene, as well as ring hydrogenation of methylphenol followed by deoxygenation.

Table 8.1 : Effect of catalyst precursors on conversion and product distribution of anthrone.

Reaction temp. (°C)	300	350	400	300	350	400	300	350	400
Catalyst Precursors	None	None	None	ATTM	ATTM	ATTM	CoMo-T2	CoMo-T2	CoMo-T2
Products (wt%)									
Anthracene	12.3	40.3	39.4	16.1	0.0	10.3	7.0	20.7	10.4
DHA	0.3	7.3	17.2	16.5	5.1	41.4	10.8	51.1	63.6
THA		0.9	6.2	0.6	27.8	30.6		4.9	23.5
THP			0.3		1.4	0.8			
sym-OHA						11.3		0.3	1.5
unsym-OHA (cis- or trans-)					9.6	1.4			0.3
unsym-OHA (trans- or cis-)					17.2	4.2			0.6
Conversion (wt%)	12.6	48.4	63.1	33.2	100	100	17.8	77.0	100

Table 8.2 : Effect of catalyst precursors on conversion and product distribution of dinaphthylether.

Reaction temp. (°C)	300	350	400	300	350	400	300	350	400
Catalyst Precursors	None	None	None	ATTM	ATTM	ATTM	CoMo-T2	CoMo-T2	CoMo-T2
Products (wt%)									
Tetralin		1.2		1.3	30.5	24.4	4.4	47.2	51.6
Naphthalene	1.9	4.1	22.9	1.4	26.1	38.3	1.9	28.6	40.2
THDNE					7.4	6.3	0.3	7.5	0.3
OHDNE					1.7			2.6	
THnaphthol					2.3	1.0		5.9	3.5
2-Naphthol			3.2		0.6	0.8	0.3	1.5	0.5
Methylphenol					0.3			0.6	0.7
Alkylbenzenes					1.9	0.9		0.5	3.1
Total conversion (wt%)	1.9	5.3	26.1	2.7	70.7	71.9	6.9	94.3	100

Table 8.3: Effect of catalyst precursors on conversion and product distribution of xanthene.

Reaction temp. (°C)	300	350	400	300	350	400	300	350	400
Catalyst Precursors	None	None	None	ATTM	ATTM	ATTM	CoMo-T2	CoMo-T2	CoMo-T2
Products (wt%)									
Methylene-biscyclohexane					0.5	1.0			3.3
CyclopentylMecyclohexane						0.7			3.1
Benzene (cyclohexylMe/Et)					1.0	8.4			2.1
Phenol (2-cyclohexylmethyl)					4.6	12.5	0.3	4.9	25.8
Benzene (1-Me-2-phenoxy)					0.6				1.1
Phenol						0.4			1.8
Methylphenol						0.9			2.7
Butylphenol					4.2	2.9	1.7	1.8	2.5
Pentylphenol					3.2	2.7	1.1	4.1	3.2
Dimethylnaphthol					1.6	1.2		2.0	4.2
Toluene						1.1			2.3
Alkylbenzenes					1.1	1.2			3.3
Conversion (wt%)	0	0	0	0	16.9	33.0	3.1	12.8	57.7

Table 8.4 : Effect of catalyst precursors on conversion and product distribution of 2,6-di t -butyl-4-methylphenol.

Reaction temp. (°C)	300	350	400	300	350	400	300	350	400
Catalyst Precursors	None	None	None	ATTM	ATTM	ATTM	CoMo-T2	CoMo-T2	CoMo-T2
Products (wt%)									
2-Butyl-4-methylphenol		44.6		55.5	13.5	0.9			
4-Methylphenol		38.8	100	23.7	66.5	24.3	71.6	97.6	85.4
Methylcyclohexane					8.2	20.2		1.6	8.5
Toluene					7.0	46.5			6.1
Phenol/other Mephenols						3.5			
Alkylbenzenes					2.1	4.7			
Conversion (wt%)	0	83.4	100	79.1	97.3	100	71.6	99.2	100

Table 8.5: Summary of results from model compound studies at 400°C.

Catalyst Precursors		None	ATTM	CoMo-T2
Total Conversion	Anthrone	63.1	100	100
Yield of deoxygenates		63.1	100	100
Total Conversion	DNE	26.1	71.9	100
Yield of deoxygenates		22.9	69.9	95.2
Total Conversion	Xanthene	0	33	57.7
Yield of deoxygenates		0	12.4	14.1
Total Conversion	DBMP	100	100	100
Yield of deoxygenates		0	71.4	14.6

Figure 8.6. Quantitative representation of anthrone reaction distribution.

Figure 8.7. Quantitative representation of dinaphthyl ether reaction distribution.

Figure 8.8. Quantitative representation of xanthene reaction distribution.

Figure 8.9. Quantitative representation of dibutylmethyl phenol reaction distribution.

In the presence of CoMo-T2, DBMP loses both butyl groups so rapidly that no BMP is isolated. Consequently, 4-methylphenol is the only product at 300°C. At 350°C some further conversion to methylcyclohexane occurs and at 400°C toluene and methylcyclohexane are produced. Although rapid dealkylation is achieved, hydroxyl removal is only slight using CoMo-T2. This suggests that CoMo-T2 may remove oxygen by hydrogenation and this pathway cannot occur rapidly until removal of other ring substituents is complete. Therefore, the presence of the stable *p*-methyl group retards the hydrogenation reaction.

Summary of Model Compound Results

Results of the model compound experiments are summarized in Table 8.5. In the absence of a catalyst precursor no oxygen removal occurs in reactions of xanthene and DBMP. All products of the non-catalytic reaction of anthrone are deoxygenated (63.1 wt%). A large proportion of the products formed from reaction of DNE, under non-catalytic conditions, are deoxygenated (22.9 wt%). For catalytic reactions with DNE and xanthene, CoMo-T2 shows a greater ability to facilitate deoxygenation than does ATTM. In the presence of ATTM, DBMP is deoxygenated to a greater extent than with CoMo-T2. Anthrone is deoxygenated completely in the presence of both precursors, although with differences in the product yields of the hydroaromatics.

CoMo-T2 shows a preference for ether cleavage facilitation, over the removal of phenolic oxygen. In the case of ATTM, the opposite appears true. In the context of coal conversion, it has been reported that ethers form a large proportion of the cross-links between aromatic moieties in mid-rank coals [4] and heterocyclic ethers have been proposed as a large contributor to the oxygen content of high rank coals [21]. The ability to remove these cross-links, without producing undesirable oxygenated products (phenols) should contribute greatly to coal conversion and product quality.

Phenols are present in almost all coals [21], and appear in great abundance in low-rank coals. From the non-catalytic reactions of DBMP, the refractory nature of the phenol hydroxy group is apparent. Great improvement in product quality may be achieved by removal of phenolic oxygens, or a reduction in their production from the reaction of other oxygen functional groups, as well as increases in conversion.

From these results ATTM should be the precursor better suited for conversion and desirable products from lower-ranked coals. Superior conversion and product distribution may be anticipated for coals of higher rank in the presence of the CoMo-T2 precursor.

Coal Liquefaction Studies

Figures 8.10-8.12 illustrate the conversion of the three coals to preasphaltenes (THF solubles), asphaltenes (toluene solubles), oils (hexane solubles) and gases. Total conversion to products is also shown.

Under non-catalytic conditions, great differences in reactivity can be observed. Wyodak exhibits a low reactivity relative to the two coals of higher rank. Illinois #6 forms increasing yields of preasphaltenes, asphaltenes and oils, whereas preasphaltenes are the most abundant products for Wyodak and Pittsburgh #8.

Total conversions are increased, in all cases, in the presence of either catalyst precursor, the most notable increase being that of the Wyodak coal using ATTM (26.6 wt% non-catalytic to 63.5 wt% ATTM). This difference is mainly attributed to greater yields of oil and gas. ATTM has very little effect on the total conversion of either the Illinois #6, or the Pittsburgh #8. Oil yields remain the same as the non-catalytic reactions, or decrease; the balance is achieved by increasing asphaltene and gas production.

A similar scenario is seen with CoMo-T2. Increases in conversion of the lower-rank coal are achieved through increased oil and gas. However, a difference is apparent when this precursor is utilized in the liquefaction of both Illinois #6 and Pittsburgh #8. Although presphaltene yields increase slightly, these increases are accompanied by greater, or equal, yields of oils and no noticable increases in gas production.

Comparison of the three coals indicates an increase in production of asphaltenes and preasphaltenes with increasing rank, under all three catalytic conditions. This is expected due to the increase in size and number of aromatic moities observed with coals of higher rank.

Conversion to oils is the most desirable result for liquefaction. However, if a large portion of these low molecular weight products are detrimental to the total product (i.e. reduction of oil stability), then a large oil yield becomes worthless. Analysis of the hexane-solubles fraction provides an estimation of the portion of the product that may be desirable (free of phenols). Figure 8.13 illustrates the size of the hexane-soluble, oil fraction, that is free of phenols. No trends are observed under non-catalytic conditions. Yields of desirable products are increased in the presence of both catalyst precursors. ATTM produced the greatest increase with the low-ranked, Wyodak coal. Whilst, with the higher ranked Illinois and Pittsburgh coals CoMo-T2 provided the larger increases in desirable product yield.

Fig. 8.10. Conversion of three coals at 400°C for 30 minutes under 7 MPa H₂.

Fig. 8.11. Conversion of three coals with ATTM under the same conditions as Fig. 8.10.

Fig. 8.12. Conversion of three coals with CoMo-T2 under the same conditions as Fig. 8.10.

Figure 8.13: Conversion to phenol-free hexane solubles for three coals under varying catalytic conditions.

CONCLUSIONS

Improvement of liquefaction product quality may be achieved by the removal of oxygen functional groups. Phenols are undesirable products of liquefaction. Therefore, their removal, or prevention of their formation, during liquefaction would be beneficial.

Model compound studies indicated that different oxygen functional groups will react differently under liquefaction conditions. The catalyst precursors under investigation facilitate deoxygenation of some model compounds to a greater extent than others. ATTM showed a preference toward phenolic oxygen removal, whereas CoMo-T2 demonstrated greater facilitation of ether cleavage.

It was predicted from the model compound results that ATTM should improve the product quality of coals with high phenol contents, by phenolic oxygen removal, and that CoMo-T2 would increase the conversion of coals with high proportions of ether linkages, or ethers within aromatic systems, and reduce formation of phenols from the reaction of these linkages.

Liquefaction studies were performed on coals of differing rank and oxygen content. ATTM improved the conversion of all the coals. Product quality from Wyodak was also improved, by increasing oil yields without a significant increase in the proportion of phenols in the oil fraction. CoMo-T2 also improved conversion of all the coals. Improvement of product quality was achieved for Illinois #6 and the Pittsburgh #8, by increasing oil formation and reducing the phenolic fraction within the oils.

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Chapter 9

Mineral Matter Effects in Low-Temperature Liquefaction of Low-Rank Coals

Introduction

Although the main interest in this project is catalytic coal liquefaction using added dispersed catalysts, it is worthy to examine the effects of mineral matters in coal. The pathways by which coal macromolecules can be depolymerised to give lighter products have long been sought by coal scientists and the precise roles of individual functional groups in the reactions which occur during liquefaction are still not clear. Depending on reaction conditions, the mineral and inorganic species present in coals can act as catalysts or poisons during liquefaction [1,2]. For example, clays, the dominant mineral species in many coals, may be possible acid cracking catalysts and pyrite, the predominant sulphide form, is a well-documented hydrogenation catalyst; however cations, common in low rank coals, block access to pores or reaction sites. Several authors have observed a favorable influence of demineralization on coal depolymerization, specifically upon removal of naturally occurring cations such as Na^+ , Ca^{2+} and K^+ [3,4]. Shams et al. [5] reported that treatment of coals with methanol and HCl removes virtually all of the calcium species, leading to retardation of the retrogressive reactions Ca was proposed to catalyze.

The aim of this work was to evaluate the nature and distribution of mineral matter in both untreated and treated (demineralized) samples of Wyodak coal, and consider the influence of these compounds by assessing their possible catalytic effect. A series of experiments has been undertaken to compare the effect of demineralization on coal conversion at low temperatures (ca 300-350°C), where preliminary results indicated that conversions were comparable upon pretreatment.

METHODS

Demineralization

Wyodak coal (DECS-8), ≤ 60 mesh, was obtained from the Penn State Coal Sample Bank; proximate and ultimate analyses are as follows [6]. Proximate analysis (as received) 32.4% vol. matter, 29.3% fixed carbon, 9.9% ash, 28.4% moisture; ultimate analysis (wt%, dmmf basis)

75.8% C, 5.2% H, 1.0% N, 0.5% S, 17.5% O. Demineralization was facilitated by successive acid treatments. The first stage was an HCl wash (10 ml per gram of coal) to remove alkaline earths which would form insoluble fluorides at the HF wash stage. This was stirred at 60°C for 1h, filtered and washed. In the second stage, a 40% HF solution (10 ml per gram of coal) was digested at 60°C for 1 hour. The final sample was thoroughly washed with distilled water to ensure removal of residual HF. The filtrate was tested with AgNO_3 to indicate the presence of any residual chloride ions.

Determination of Inorganic and Mineral Phase Distribution

Both coal samples were analyzed by ICP-AAS and CCSEM to more clearly identify the changes in inorganic element and mineralogical phase distribution upon acid. Samples were ashed at 950°C and the ash dissolved using lithium metaborate fusion. Solutions were then analyzed using an inductively coupled plasma spectrophotometer (ICP). For CCSEM, coals were ground to -200mesh and the samples mounted in an epoxy resin. The sample is scanned with an electron beam to locate bright spots which correspond to mineral or ash species. Integrated software classifies the minerals into categories based on size and composition.

Liquefaction

Demineralised coal samples were vacuum dried at 110°C for 2h prior to use. Liquefaction was carried out in a 25 ml stainless steel microautoclave with *ca* 4g coal, at 300 and 350°C, 1000 psi H₂ or N₂ for 30 min. When solvent was present, the coal:solvent ratio was 1:1 w/w; both H-donor (tetralin) and non-donor solvents (1-methylnaphthalene) were utilized. Gaseous products were collected and analyzed by GC; liquid and solid products were recovered and separated by sequential Soxhlet extraction into *n*-hexane solubles (oils), toluene solubles (asphaltenes) and THF solubles (preasphaltenes). The THF-insoluble residue was washed with acetone followed by *n*-pentane to remove residual THF. All products were dried under vacuum at 110°C for *ca* 10h. The conversion of coal into soluble products and gases was calculated on the basis of recovered THF-insoluble residue and reported on a dmmf basis.

¹³C NMR

Solid state ¹³C NMR spectra of the normal and demineralized coal samples and their associated THF-insoluble residues were recorded on a Chemagnetics M-100 NMR spectrometer using the cross polarization magic angle spinning (CP-MAS) technique. The measurements were carried out at a carbon frequency of 25.1 MHz.

FTIR

Fourier transform infrared (FTIR) spectra of the demineralised coal and liquefaction residues were recorded on a Digilab FTS-60 spectrometer by co-adding 400 scans at a resolution of 2 cm⁻¹. The samples were prepared as KBr discs; predried sample (3 mg) was mixed with KBr (300 mg). All spectra were baseline corrected.

Results and Discussion

ICP-AAS

As summarised in Table 9.1, metal concentration was determined by ICP-AAS in the normal and demineralised Wyodak coal samples. Ash concentration was determined as 8.94 wt%,

falling to *ca* 0.37 wt% upon demineralization, with the corresponding metal concentrations as indicated. All values are expressed in weight percent on an coal basis.

TABLE 9.1. Inorganic Elemental Analysis of Normal and Demineralised Wyodak Coal Samples by ICP-AAS.

Sample	Ash	Metal Concentration (wt%, coal basis)				
		Fe	Ca	Mg	Na	K
Normal	8.94	0.49	1.18	0.27	0.10	0.07
Demineralised	0.37	0.21	0.03	0.006	7×10^{-4}	9×10^{-4}

CCSEM

Table 9.2 summarises the mineral phase distribution in both the normal and acid digested coal samples. Results are expressed on a weight % coal basis. As anticipated, clays were the predominant mineral phase in the initial coal sample. Upon acid treatment, all mineral species concentrations were significantly reduced.

TABLE 9.2. Mineral Concentrations of Normal and Demineralised Wyodak Coal Samples by CCSEM.

Mineral	Composition (wt%, coal basis)	
	Wyodak	Wyodak (demin)
Montmorillonite	4.15	-
Na Al silicate	2.20	0.0016
Aluminosilicate	1.32	0.07
Kaolinite	0.92	0.014
Barite	0.8	0.006
Quartz	0.78	0.012
Pyrite	0.58	0.018

Liquefaction Data

Results for the reactions conducted at 350 °C, both in the presence and absence of solvent, are reported in Table 9.3 and Figure 9.1. These will be discussed with respect to data with untreated Wyodak coal [7]. Clearly, demineralization imparts no seriously detrimental effects on liquefaction under such conditions.

TABLE 9.3. Results of Non-Catalytic Liquefaction of Normal and Demineralised Wyodak Coal at 350 °C for 30 min. Under 6.9 MPa H₂.

Pretreatment	Solvent	Product Distribution (% dmmf basis)				
		Gas	Oil	Asph	Preasph	% Conv.
-	-	3.3	2.1	2.6	4.5	12.5
demineralised	-	10.0	0.8	0.4	5.3	16.6
-	Tetralin	4.2	4.1	7.6	10.0	25.9
demineralised	"	12.0	7.1	6.3	14.4	40.3
-	1-MN	4.0	1.1	5.8	7.4	18.3
demineralised	"	7.7	5.6	3.3	10.3	26.9

Figure 9.1. Results of Non-Catalytic Liquefaction of Normal and Demineralised Wyodak Coal at 350 °C for 30 min. Under 6.9 MPa H₂.

TABLE 9.4. Results of Non-Catalytic Liquefaction of Demineralised Wyodak Coal at 350 °C for 30 min. Under 6.9 MPa H₂ and N₂.

Gas	Solvent	Product Distribution (% dmmf basis)				
		Gas	Oil	Asph	Preasph	% Conv.
H ₂	-	10.0	0.8	0.4	5.3	16.6
N ₂	-	10.7	1.2	0.7	5.2	17.8
H ₂	Tetralin	12.0	7.1	6.3	14.4	40.3
N ₂	"	10.4	10.3	3.6	17.8	42.1
H ₂	1-MN	7.7	5.6	3.3	10.3	26.9
N ₂	"	8.7	5.8	1.4	8.4	24.4

The overall conversions and liquid product distribution indicate that the most significant changes occur in the presence of solvent, both H-donor and non-donor. In the absence of solvent, conversion is solely due to pyrolysis, i.e. there are no solvent dissolution or H donation contributions. Higher conversion is the result of increased gas yield rather than liquid yield. This may be derived from two contributions. If the reduction in Fe concentration, as highlighted by ICP, also comprises pyrite, this would account for the decrease in liquid yield. Moreover, as the increased gas make is due to CO₂, removal of the mineral matter may be considered to promote more facile pyrolysis of -COOH versus -COO-M⁺. This confirms model compound studies conducted by Eskay et al. [8] who reported that the salts of carboxylic acids do not readily undergo decarboxylation at 400°C and should therefore be stable at the reaction temperature of 350°C used here.

Reaction in the presence of the non-donor solvent, 1-methylnaphthalene (1-MN), results in increases in both gas and liquid yield relative to the no-solvent situation. With "normal" coal and 1-MN, the increase in liquid yield for the raw coal is 5.1%. Presumably this increase is the "extra" liquid dissolved out by the solvent. With demineralised coal and 1-MN, the increased liquid yield is 12.4%. The solvent is better able to dissolve material from the demineralised coal. This suggests that there is improved access of the solvent to the coal interior upon removal of mineral species. Swelling of the samples in pyridine provided confirmation of this; the swelling ratios of the normal and demineralised samples in pyridine were 2.18 and 2.9, respectively.

The best liquid conversion, defined by oil concentration as a fraction of the total liquid yield, occurs upon reaction with tetralin. This is not surprising given that tetralin is an H donor, thus any enhancement in tetralin conversion relative to 1-MN can be attributed to H donation. The increase in liquid yield for normal coal in tetralin, relative to 1-MN, is 7.4%; the increase for demineralised coal is 8.6%. The difference in these numbers is within experimental error, $\pm 3\%$, hence demineralization has no effect on H transfer from tetralin and there is no mineral matter catalysis of H donation.

Table 9.4 and Figure 9.2 summarise the results of liquefaction conducted under N_2 and those in H_2 . No significant deviation in overall conversion or product distribution was observed, even in the presence of solvent.

Figure 2. Results of Non-Catalytic Liquefaction of Demineralised Wyodak Coal at 350 °C for 30 min. Under 6.9 MPa H_2 and N_2 .

There are similarities between the results presented here and those of other studies, not necessarily limited to demineralised samples. Tomic and Schobert [9] also observed solvent effects under mild liquefaction conditions of subbituminous coals; solvent addition enhanced conversion relative to the reaction with no solvent, similar to the results in Table 9.3. If pyrite concentration has been reduced, the results in Table 9.4 confirm those reported by Tomic and

Schobert [9], Artok [10] and Huang [11] who similarly reported that utilization of $H_2(g)$ is ineffective without a good hydrogenation catalyst, as illustrated by the similarities in the comparative H_2 and N_2 runs. Serio et al. [3], also reported enhanced conversion for low rank coals following demineralization. This raises questions as to possible contribution of mineral species to low temperature liquefaction mechanisms. Joseph [4] ascribed this phenomenon to cations inhibiting hydrogen transfer from donor solvent/gaseous hydrogen to free radicals, in effect promoting retrogressive reactions. It could be that the absence of these species allows for better access to reactive sites in the coal interior.

Solid State ^{13}C NMR

The ^{13}C CP-MAS spectra of the normal and demineralised coal are shown in Figure 9.3. The ^{13}C CP-MAS spectrum of the demineralised Wyodak displays many similarities to that of the untreated coal. The region between 0 and 80 ppm consists primarily of aliphatic carbons, e.g. methoxy groups. The second region of interest between 90 and 170 ppm is due to aromatic carbon. The shoulders on the side of the aromatic band may be attributed to specific functionalities, e.g. catechol groups (at 142 ppm) and phenolic groups (at 152 ppm). The carboxylic functionality is prominent at 180 ppm, similarly for the carbonyl at *ca* 210 ppm. In the aliphatic band, the symmetry observed for the parent coal is lost, and the appearance of a shoulder at ~25 ppm is observed. This may be attributed to a number of groups, including CH_3 -Ar side chains (20-21 ppm). Furthermore, the distinct shoulders observed in the aromatic region have virtually disappeared, indicating a loss of oxygen functionalities.

Figure 9.3. ^{13}C CP-MAS Spectra of (a) Normal and (b) Demineralised Wyodak Coal.

Figure 9.4. FTIR Spectra of THF-Insoluble Residue from Reaction of Demineralised Wyodak Coal in (a) Absence of Solvent, (b) Presence of Tetralin and (c) Presence of 1-MN.

FTIR

Comparative FTIR spectra of the normal and demineralised coal and associated residues from reaction at 350°C under H₂ are shown in Figure 9.4. After reaction under H₂ at 350°C, the most notable feature of the whole product spectrum is a decrease in hydroxyl concentration, in part attributed to a loss of H₂O. Further examination of the THF-insoluble residues from these experiments indicates little difference between the composition of the residues, from both the normal and demineralized samples reacted under H₂ in the presence and absence of solvent. The FTIR spectrum of the THF-insoluble residue from the reaction conducted with tetralin displays somewhat contrasting features. The carboxyl stretching region is much broader; moreover, the ester shoulder is more pronounced and the carbonyl region is much more defined. Similarly, the FTIR spectra of the THF-extracted raw coal and the residues from the runs conducted at under N₂ demonstrated that under all conditions, i.e. both in the presence and absence of solvent, no marked changes were observed.

Conclusions

Relative to runs at 350°C with untreated coal, demineralization affords higher overall conversions; this increase in conversion is the result of increased gas make over soluble products. This trend becomes more apparent when either an H-donor (tetralin) or non-donor (1-MN) solvent are used. Specifically, there is no evident mineral matter effect on solvent H donation acting only in solvent capacity. Comparison of the two sets of data suggests that the reactions undergone at 350°C are not mineral matter catalyzed. Indeed, the main effect of the acid treatments reported here is to open the coal structure, thus promoting more intimate contact between the solvent and the coal interior.

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Chapter 10

Effect of Water Addition on In-Situ Generated MoS₂ Catalyst for C-O Bond Cleavage and Hydrogenation of 2,2'-Dinaphthyl Ether

Introduction

In our recent work, we found a strong promoting effect of water on low-severity catalytic coal liquefaction using molybdenum sulfide catalyst in-situ generated from ammonium tetrathiomolybdate (ATTM): addition of water increased the conversion of Wyodak coal using ATTM as a catalyst precursor at 350 °C from 29.5 to 66.5 wt% [1]. Initially, this strong promoting effect of water was surprising to us, because it has been shown that better drying method for moisture removal results in higher coal conversion in catalytic liquefaction using molybdenum sulfide catalyst [2]. It was also observed that addition of water to catalytic coal hydroliquefaction has negative effect [3-5]. On the other hand, water addition to non-catalytic coal conversion reactions and some model reactions has been shown to have positive impacts [6-10]. More recently, it has been reported that ether compounds such as 1-phenoxy-naphthalene and 9-phenoxyphenanthrene cleave in water at 315 °C, and this cleavage is enhanced at higher temperature; since water becomes a stronger acid as temperature increased, this cleavage reaction proceeds through ionic process [9,10].

In the present study, in order to clarify the role of water in catalytic hydroliquefaction of coal, we carried out hydrogenation and hydrogenolysis of 2,2'-dinaphthyl ether (DNE) using ATTM as a catalyst precursor in the absence and presence of H₂O or D₂O. There are many connecting linkages in coal structures; the aromatic C-O and aromatic-aliphatic C-C bonds are believed to be important linkages between aromatic moieties of coal structures. Therefore, in order to increase the conversion of coal to liquids, it is necessary to cleave these connecting linkages. Coal structures have not been clarified at the molecular level. The use of coal-related model compounds is suitable for understanding fundamental chemistry. The products from the hydrogenation of model compounds can be easily identified by GC/MS. DNE has been shown to be thermally unreactive in the absence of catalyst, but its conversion is enhanced by some metal sulfide catalyst [11]. Here we used DNE to investigate the effect of the addition of water on cleavage of ether-linkages and on hydrogenation of aromatic rings using ATTM under the conditions of coal liquefaction.

Experimental Section

Preparation of Catalyst Precursor

Ammonium tetrathiomolybdate (ATTM) were purchased from Aldrich, and 2,2'-dinaphthyl ether (DNE) from TCI America. DNE and ATTM were used without further purification. It was noted in previous work in this laboratory that long-time storage of ATTM in reagent vials in air may lead to degradation of the reagent, which results in deviations in the activity of in-situ generated MoS₂ catalyst from different bottles of ATTM reagent. In this work, a bottle of newly purchased ATTM was used in all the experiments on DNE runs, and the reagent bottle was stored in a refrigerator in order to minimize oxidative degradation.

Model Compound Reactions

A horizontal tubing bomb microautoclave reactor with a capacity of 25 mL was loaded with ca. 0.216 g DNE, 1 wt% catalyst precursor (1 wt % Mo based on DNE) and 1.47 g solvent (tridecane). When water was added, the weight ratio of H₂O to DNE was 0.56, unless otherwise mentioned. The reactor was purged four times with H₂ and then pressurized with 6.9 MPa H₂ at room temperature for all experiments. A preheated fluidized sand bath was used as the heating source, and the horizontal tubing bomb reactor was vertically agitated to provide mixing (about 240 strokes/min). After the reaction the hot tubing bomb was quenched in a cold water bath. The contents were washed with 30 - 40 mL acetone through a low speed filter paper for qualitative and quantitative GC analysis of the filtrate. Two-step reaction was also carried out in a similar manner as described above, except that the active MoS₂ catalyst was prepared first using ATTM with and without H₂O in the first-step reaction, and subsequently, the reactor was opened, and DNE was then added into the reactor. DNE was treated with and without H₂O as the second-step reaction.

The products were identified by GC-MS using a Hewlett-Packard 5890 II GC coupled with a HP 5971 A mass-selective detector operating at electron impact mode (EI, 70 eV). The column used for GC-MS was a J&W DB-17 column; 30-m X 0.25-mm, coated with 50% phenyl 50% methylpolysiloxane with a coating film thickness of 0.25 μ m. For quantification, a Perkin Elmer 8500 GC with flame ionization detector and the same type of column (DB-17) was used. Both GC and GC-MS were programmed from 80 to 280 °C at a heating rate of 4 °C/min and a final

holding time of 8 min. The response factors for 5 of the products were determined using pure compounds.

Determination of Response Factor

Response factors of the components were calculated equation shown below.

$$\text{Response factor} = [(A_j/M_j) / (A_{isd}/M_{isd})] \times 1.05;$$

Mass of internal standard (n-Dodecane): M_{isd}

Peak Area (area%) of internal standard in GC: A_{isd}

Mass of component j: M_j

Peak Area (area%) of component j in GC: A_j

GC analysis was carried out under the conditions shown below;

Injection volume: 1.0 μ l

Split or Splitless: Split

Injection Temperature: 280 °C

Detector Temperature: 290 °C

Initial Temperature: 80 °C

Rate of Heating: 4 °C/min.

Final Temperature: 280 °C

Holding Time: 10 min.

When yields of the products are calculating by using response factor, the recovery of the products were sometimes low about from 90 to 95 wt%. Therefore the effect of products concentration in solution on the response factor is investigated. The response factor of the product except for DNE do not change with changing the concentration in solution, but the response factor of and DNE changes. Figure 1 shows the relationship between the response factor and the peak height of DNE in GC chromatograms. At lower concentration than 50 μ V of peak height of DNE, the response factor follows equation (1), and At higher than 50 μ V of peak height, it follows equation (2).

$$y = 8.91 \times 10^{-3}x + 0.691 \quad (1)$$

$$y = 9.54 \times 10^{-4}x + 0.5579 \quad (2)$$

So the response factor of DNE was calculated by these equations.

Fig.1 Relationship between gc response factor of dinaphthyl ether (DNE) and DNE peak height in gas chromatogram (DNE concentration in solution)

Results and Discussion

One-Step Reaction

Table 10.1 shows the results of non-catalytic and catalytic runs of DNE with in-situ generated dispersed MoS₂ catalysts at 350, 375 and 400 °C. Without ATTM, the conversions of DNE are very low, even at 400 °C. Adding water alone seems to inhibit the conversion of DNE completely. However, in the presence of ATTM conversions are significant. An addition of water to the runs with ATTM substantially increase the conversion of DNE. Upon addition of water to the catalytic runs, the conversion of DNE increases from 46.0 % to 83.8 % at 350 °C. The principal products are tetralin, naphthalene, 2-naphthol, 5,6,7,8-tetrahydro-2-naphthol, octahydroDNE, and tetrahydroDNE. Formation of these products suggests that both the ether linkage cleavage reaction and hydrogenation of aromatic rings occur simultaneously. Because the yield of tetralin is higher for the runs with added water than for those without water, the hydrogenation of aromatic ring prevails in the run with water and ATTM.

Table 10.1 Effect of addition of H₂O on reactions of DNE at 350-400 °C under 6.9 MPa H₂.

Run #	16	17	15	19	18	20	7	6	8	5	3	4
Catalyst Precursors	None	None	None	H ₂ O	H ₂ O	H ₂ O	ATTM	ATTM	ATTM	ATTM + H ₂ O	ATTM + H ₂ O	ATTM + H ₂ O
Temperature (°C)	350	375	400	350	375	400	350	375	400	350	375	400
DNE Conversion (mol %)	0.7	0.5	4.6	0.0	0.0	0.0	46.0	86.4	82.4	83.8	95.2	94.2
Products (mol %)												
Tetralin		0.7	5.4				31.4	70.9	66.7	72.7	106.1	109.1
Naphthalene		0.3	2.0				33.1	74.1	73.4	57.1	66.2	70.8
5,6,7,8-Tetrahydro-2-naphthol							8.0	6.2	3.6	8.1	9.5	6.0
2-Naphthol							2.2	4.7	12.6	3.4		
OctahydroDNE			0.3				1.3	2.0	1.0	2.5	2.2	
TetrahydroDNE	0.6		0.6				7.4	6.5	3.2	10.6	2.1	1.2

In order to clarify the role of water, DNE was hydrogenated with ATTM and D₂O. Because aryl ethers cleave in H₂O at high temperature above 315 °C through ionic mechanism [5], this ionic effect of H₂O on the cleavage of C-O bond in DNE is investigated. Even though water alone has inhibition effect on conversion of DNE as described above. Table 10.2 represents the results of catalyst run of DNE with dispersed catalysts and H₂O or D₂O at 350, 375 and 400 °C. Comparing the results using H₂O and D₂O, the conversions of DNE are almost the same in each pair of corresponding runs. There are no apparent isotopic effect on the conversion of DNE and the yields of the products. The results of GC/MS analysis indicate that the products and recovered DNE contained a few deuterium atom, and the fragmentation of mass spectra of the products indicate that deuterium atoms were introduced into the products unselectively. These results show that the hydrogen from water has a little effect on the conversion of DNE. In other words, we have found no clear evidence that H₂O enhanced ether bond cleavage: the ionic effect of water on cleavage of ether-linkage in DNE is not significant.

Table 10.2 Catalytic reactions of DNE using ATTM and H₂O or D₂O at 350-400 °C under 6.9 Mpa H₂

Rnu #	29	5	32	3	27	4
Catalyst	ATTM + D ₂ O	ATTM + H ₂ O	ATTM + D ₂ O	ATTM + H ₂ O	ATTM + D ₂ O	ATTM + H ₂ O
Temperature(°C)	350	350	375	375	400	400
Conversion (mol%)	82.9	83.8	95.5	95.2	95.6	94.2
Compound identified (mol%)						
Tetralin	68.8	72.3	106.5	106.1	106.5	109.1
Naphthalene	59.7	57.2	71.2	66.2	64.7	70.8
5,6,7,8-Tetrahydro-2-naphthol	7.9	8.0	9.0	9.5	6.6	6.0
2-naphthol	2.2	3.2			1.1	
OctahydroDNE	2.4	3.1	0.7	2.2	1.1	
TetrahydroDNE	11.2	11.3	1.5	2.1	1.2	1.2

Two-Step Reaction

As shown in Tables 10.1 and 10.2, the conversion of DNE increases with an addition of water. In order to clarify the role of addition of water on the hydrogenation of DNE further, two-step reaction was carried out. In the first-step, the Mo sulfide catalyst was prepared from

decomposition of ATTM in the presence and the absence of water at 350, 375 and 400 °C under hydrogen pressure for 30 min. Subsequently the reactor was quenched, vented, and opened to allow the loading of DNE followed by purge and repressurization with H₂. The hydrogenation of DNE, as the second-step, was carried out with and without H₂O at 350 °C under hydrogen pressure for 30 min. Table 10.3 shows the results of the two-step reactions. Using the catalyst prepared from ATTM alone at 350, 375 and 400 °C, the conversions of DNE are almost the same at 64-67 %: the activities of the catalysts are very similar. However, highly active catalysts are generated from ATTM with added H₂O, the conversion of DNE is the largest at 375 °C: the catalyst prepared at 375 °C is most active. This result is as same as our previous one[12]. After the preparation of catalyst, the addition of water decreases the conversion of DNE. For example the conversion of DNE decreased from 64.4 % to 32.9 % at 350 °C (first-step) after the addition of water to the second-step run. In addition, after the preparation of catalyst from ATTM and water at 350 °C complete removal of water caused about 100 % conversion of DNE at 350 °C at the second-step. These results suggest that water itself does not have promoting effect on hydrogenation of DNE, but that it is effective for the preparation of good catalyst for hydrogenation and bond cleavage of DNE.

Table 10.3 Two-step reactions of DNE under 6.9 MPa H₂.

Experiment #	44	48	49	41	42	51	68	67	50	96*
Temperature(°C) 1st	350	375	400	350	375	400	350	375	400	350
Temperature(°C) 2nd	350	350	350	350	350	350	350	350	350	350
First Catalyst	ATTM	ATTM	ATTM	ATTM + H ₂ O	ATTM + H ₂ O	ATTM + H ₂ O	ATTM	ATTM	ATTM	ATTM + H ₂ O
Second Addition	None	None	None	None	None	None	H ₂ O	H ₂ O	H ₂ O	None
Conversion (mol %)	64.4	66.7	66.0	82.7	96.0	76.9	32.9	29.7	41.2	97.0
Products (mol%)										
Tetralin	49.1	46.9	44.7	58.6	76.5	53.1	26.8	22.9	31.9	89.6
Naphthalene	67.5	72.6	72.6	79.5	85.1	75.9	26.6	25.5	39.5	104.4
Tetrahydronaphthol	0.8	0.6	1.0	1.4	1.6	4.2	1.2	0.6	0.7	
2-naphthol	0.8	0.6	1.0	0.4	0.1	2.2	1.6	0.8	1.0	
OctahydroDNE	0.3	0.3	0.4	0.8	2.1	0.7	0.2	0.2	0.2	
TetrahydroDNE	5.1	6.1	6.0	12.0	12.2	8.5	4.6	4.6	4.4	

* After the first-step reaction, water was completely removed by venting at 200 °C for 35 min., prior to the addition of DNE for second-step reaction.

Hand-Shaking Effect

While carrying out two-step reactions, we found a strange hand-shaking effect on the conversion of DNE: before starting a second-step run, a reactor which contained DNE was shook by hand above three hundred times, and the conversion of DNE increased. As shown below, because with below one hundred times hand-shaking the conversion of DNE was still low, we shook the reactor above three hundred times. Table 4 shows the results of the hand-shaking effect. In all runs, the conversions of DNE are higher with hand-shaking than without hand-shaking and with one hundred times hand-shaking: the conversion of DNE improves from 10 % to 40% with hand-shaking for all runs. Without hand-shaking we cannot find the relationship between the conversion of DNE and temperature for catalyst preparation using only ATTM (first-step), but with hand-shaking it is clear that the conversions at 350, 375, 400 °C is almost the same. Therefore we used the hand-shaking for all two-step reactions described in Table 10.4.

Table 10.4 Hand shaking effect between first and second reactions on conversion of DNE and yields of products.

Experiment #	60	44	59	48	53	49	38	41	39	42	40	51
First-step Catalyst	ATTM	ATTM	ATTM	ATTM	ATTM	ATTM	ATTM + H ₂ O	ATTM + H ₂ O	ATTM + H ₂ O	ATTM + H ₂ O	ATTM + H ₂ O	ATTM + H ₂ O
Temperature (°C) 1st	350	350	375	375	400	400	350	350	375	375	400	400
Second-step addition	None	None	None	None	None	None	None	None	None	None	None	None
Temperature (°C) 2nd	350	350	350	350	350	350	350	350	350	350	350	350
Hand Shaking	-	+	-	+	-	+	-	+	+	+	-	+
Shaking Times		over 300		over 300		over 300		over 300	under 100	over 300		over 300
Conversion (mol %)	45.0	64.4	26.4	66.7	56.6	66.0	46.0	82.7	73.9	89.4	50.0	76.9
Products (mol%)												
Tetralin	31.3	49.1	20.4	46.9	38.9	44.7	29.5	58.6	47.4	76.5	32.1	53.1
Naphthalene	45.8	67.5	23.1	72.6	59.8	72.6	37.4	79.5	79.1	86.2	50.5	75.9
5,6,7,8-Tetrahydro-2-naphthol	0.8	0.8		0.6	0.4	1.0	1.4	1.4	3.1	3.2	1.5	4.2
2-Naphthol	0.8	0.8	0.1	0.6	0.2	1.0	1.4	0.4	3.2		0.5	2.2
OctahydroDNE	0.4	0.3	0.2	0.3	0.3	0.4	0.2	0.8	0.5	0.8		0.7
TetrahydroDNE	5.3	5.1	4.3	6.1	6.6	6.0	7.2	12.0	6.9	5.7	7.7	8.5

Effect of H₂O/ DNE Ratio

In the test discussed above, the weight ratio of H₂O/DNE was maintained at 0.56 for the determination of role of water addition on hydrogenation of DNE. We have determine the optimum amount of added water. This was done by examining the relationship between the conversion of DNE and amount of added D₂O. Figure 10.2 shows the relationship between the amount of D₂O addition and the conversion of DNE from the runs at 350 °C for 30 min. Figures 10.3 and 10.4 also show the relationship between DNE conversion and weight ratio of D₂O/DNE and that of D₂O/ATTM, respectively. Because the trend of the change of DNE conversion on the amount of added D₂O is the same of those both on the weight ratio of D₂O/DNE and D₂O/ATTM, we will discuss on the relationship between DNE conversion and the amount of added D₂O. The conversions of DNE gradually increase from 46 % to 100% with increasing water amount from 0 to 0.2 g corresponding to a D₂O/DNE weight ratio of about 0.93, and they decrease from 100% to 60 % with further addition of water. These results also clearly indicate that 0.026 of the ratio of ATTM to D₂O is optimum for conversion of DNE under the conditions employed. It seems that since water is used for the preparation of effective catalyst from ATTM, the conversion of DNE is large up to 0.235 g of D₂O. However water itself has a negative effect for the hydrogenation of DNE, further additions of D₂O over 0.235 g seem to cause the decrease of the conversion of DNE.

Fig. 10.2 Effect of addotion of D₂O on conversion of 2,2'-dinaphthyl ether (DNE) at 350 °C for 30 min. in 25 mL reactor. DNE: 0.216g; ATTM: 0.006g; n-C₁₃: 1.47g

Fig. 3 Relationship between weight ratio of D₂O/DNE and DNE conversion at 350 °C for 30 min in 25 mL reactor. DNE: 0.216g; ATTM: 0.006g; n-C13: 1.47g

Fig. 4 Relationship between weight ratio of D₂O/ATTM and DNE conversion at 350 °C for 30 min in 25 mL reactor. DNE: 0.216g; ATTM: 0.006g; n-C13: 1.47g

Conclusions

A proper amount of added water has a strong promoting effect on hydrogenation and hydrogenolysis of DNE using molybdenum sulfide catalyst in-situ generated from ATTM. We have found that the addition of water is not effective for DNE conversion, but is effective for the preparation of active catalyst from ATTM for hydrogenation and hydrogenolysis of DNE.

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Chapter 11

High-Temperature Simulated Distillation GC Analysis of Heavy Liquids and Their Products from Catalytic Upgrading

Introduction

This work is a part of our effort to establish a method for analyzing the liquids from coal/petroleum coprocessing and coal liquefaction. In order to facilitate the analytical work of both the starting materials and the upgrading products, we have used petroleum residue. Residues of petroleum distillation, also called resids, are referred to as the bottom of the barrel and include two types of distillation tower bottoms. The term atmospheric resid generally describes the material remaining at the bottom of the atmospheric distillation tower which has an upper boiling limit of about 340°C; the term vacuum resid refers to the bottom of a vacuum distillation which has an atmospheric equivalent boiling point range of above 540°C [1].

The main purpose of petroleum resid upgrading is to reduce the boiling point range as well as to remove sulfur, nitrogen and metals from resids. Hydroprocessing is one of the important ways of resid upgrading. It is necessary to characterize resids and their products with various techniques that indicate their compositional features. Because petroleum resids are complex mixtures which contain hundreds of compounds with high molecular weights, characterizing resids is a tedious and complicated task. Laboratory-scale distillation tests are widely used for determining boiling point range of crude oil and their products [2]. However, highly refined data by using this method would require tremendous amounts of time and labor. Furthermore, the boiling point range that can be determined by laboratory distillation operation is limited, particularly for resids.

Simulated distillation analysis by gas chromatography (SimDis GC) is an effective method which requires about one hour for each test. SimDis GC analysis achieved ASTM standard status in 1973 under the designation of D2887 and was revised three times in 1984, 1989 and 1993. ASTM D5307 was defined in 1992 for determining the crude oil boiling point range. However, these methods can only be applied to fractions with final boiling point up to 538°C (1000°F) [3,4]. Consequently, there are various techniques being tested in order to determine the boiling point distribution of heavy resids. Padlo and Kugler studied SimDis by HPLC equipment using an evaporative light scattering detector [5]. Bacaud et al. performed modeling based on simulated distillation to evaluate the hydroprocessed resids [6]. Klein and coworkers used SimDis results as a part of analytical data for resid structure modeling [7].

High-temperature simulated distillation using GC (HT-SimDis GC) has become possible recently due to the development of thermally stable wide bore capillary columns. Such open tubular columns offer a number of advantages over packed columns [8]. Some of the advantages are: better column stability and life, lower column bleed, faster analysis, elution of high boiling petroleum fractions, compatibility with automated on-column injection, and improved reproducibility. However, HT-SimDis GC has not been widely used, and no standard method is available for resids. We have established a method in our laboratory for HT-SimDis GC analysis of petroleum resids, which covers the high end of atmospheric equivalent boiling point, up to 847°C (1557°F). This report presents our results on HT-SimDis GC analysis of two resids and their products from laboratory tests of catalytic hydroprocessing. Herein below the term resid refers to the feedstock, and the term residue refers to the uneluted (undistillable) portion of the resid in HT-SimDis GC.

Experimental

Solvent extraction

Two petroleum resids, an atmospheric resid (AR) and a vacuum resid (VR2), were used in this study which were obtained from Garyville Refinery of Marathon Oil Company. Their elemental compositions are as follows: for AR, C: 84.64; H: 11.14; S: 3.87; N: 0.23, O (by difference): 0.12 wt%; and for VR2, C: 83.20; H: 9.83; S: 5.01; N: 0.54, O (by difference): 1.42 wt%. The contents of asphaltenes, which are defined as hexane-insoluble but toluene-soluble fraction of resid, were estimated for AR and VR2 through n-hexane and toluene solubilities. In order to do this estimation, 4 gram of AR or VR2 resid was dissolved in 400 mL hexane in ultrasonic bath for 1 hour and then filtered with 0.45 μm (pore size) membrane filter. The solid on filter paper was dried and weighed as hexane insoluble (HI) material. Similar procedure was used with toluene to determine the toluene insolubles (TI). The amounts of asphaltenes in AR and VR2 were determined from the difference of hexane and toluene insolubles.

High-temperature simulated distillation GC

HT-SimDis GC was performed using Hewlett-Packard Model 5890 II Plus GC with a flame ionization detector and temperature programmable cool on-column injector from which it is possible to introduce a liquid sample directly into the head of the column. On-column injection avoids sample discrimination and decomposition which can occur in heated inlets that rely on flash vaporization [8]. The injector temperature was always maintained 3°C higher than column temperature during entire analysis. Exact amount of sample was injected with an automatic sampler, which maximizes the reproducibility. Programming the chromatographic oven to above 400°C can cause a considerable drop in capillary column flow rate, which is caused by increasing carrier gas viscosity as the oven is programmed to higher temperatures. To avoid this effect, the GC on-column flow system is operated in a total flow control mode. It was possible because our chromatograph is equipped with a controller capable of either maintaining carrier gas flow constant

or the inlet pressure constant. In this study we maintained the carrier (He) flow constant (10.6 mL/min). The velocity of the carrier gas flow is 79.2 cm/second. A high-temperature aluminium clad megabore capillary column (HT5 phase consisting of Carborane, 6 m length, 0.53 mm I.D., 0.78 mm O.D., and 0.1 μ m film thickness) from SGE supplied by Supelco Inc. was used for HT-SimDis GC analysis. A computer-based chromatography data system (Hewlett-Packard ChemStation software, B.02.04) was used for data acquisition. To obtain corrected area of sample from the baseline drift and signal offset, the column compensation was performed and stored to do subtraction and give the right values. The SimDis Expert software (V 5.0) provided by Separations Systems Co. was used for post-run data analysis of HT-SimDis.

Prior to the injection, the samples were diluted with CS₂ to about 2 wt%. High purity CS₂ was used as a solvent because resids are completely miscible in it and it has a low boiling point and only a slight response with FID. The injection volumes were 1.0 μ L. The calibration standard containing n-paraffins (C₅-C₁₀₀) was prepared by dissolving liquid n-paraffins mixture (C₅-C₂₀) and polywax (Polywax 655) in CS₂ under IR lamp in a sealed vial. The individual compounds used for comparison of their true boiling point with the boiling points obtained from HT-SimDis GC analysis were reagent-grade chemicals obtained from commercial suppliers. High boiling point lube oil standard (supplied by Separation Systems) was used as a reference standard to check the HT-SimDis GC calibration; it was used as an external standard for estimating the uneluted portion (undistillable residue) of the resids and their products.

Four different sets of GC conditions were tested in screening analysis. After the conditions have been set to meet performance requirements, the column was conditioned; the blank run was then conducted and the data stored for column compensation. Using the same conditions as for the blank run, appropriate aliquot of the calibration mixture was injected to obtain a retention time versus boiling point calibration. In general, the volume of the calibration mixture injected must be selected to avoid distortion of any component peak shapes caused by overloading the sample

capacity of the column. Distorted peaks will result in the erroneous retention times and hence errors in boiling point determination. The calibration curve (retention time of each peak versus the corresponding boiling point of the component) should be essentially linear. Our calibration has been always linear in the range between C₁₀ and C₉₄ paraffin which has a boiling point of 704°C. It was assumed that the calibration is linear beyond that point. Once calibration is ready, it is then verified with reference standard. We have also measured boiling points of several types of pure model compounds (cycloalkanes, aromatics, heteroatom-containing compounds) to compare with their true boiling points.

Both external standard and real samples were prepared after allowing them to reach room temperature (if they were stored in refrigerator) to make them homogeneous. The exact amounts were weighed and dissolved in given amounts of CS₂ in order to obtain about 2 wt% solution in CS₂.

The external standard and resid samples were analyzed separately using exactly the same conditions that were used in the blank and calibration runs. Exactly 1 µL of diluted samples and external standards were injected using auto sample injector and data collected. Once the total corrected cumulative area of external standard and samples are available, the residue (uneluted portion of the samples) is estimated using the principles of calculations given below:

$$W_E = M_E / (M_C + M_E);$$

Where W_E = Weight fraction of external standard,

M_E = Wt. of external standard, and

M_C = Wt. of solvent CS₂.

$$W_S = M_S / (M_C + M_S);$$

Where W_S = Weight fraction of resid sample,

M_S = Wt. of resid sample, and

M_C = Wt. of solvent CS₂.

$$\text{ESAM} = 100 \times (A_S/A_E) \times (W_E/W_S);$$

Where ESAM = Eluted portion (distillable) of the resid sample in wt%,

A_E = Cumulative GC peak area of external standard of 1 μL injection, and

A_S = Cumulative GC peak area of resid sample of 1 μL injection.

$$\text{RES} = 100 - \text{ESAM};$$

Where RES = Uneluted portion (residue) of the resid sample in wt%.

Once the percentage of eluted portion of resid sample is estimated, the boiling point distribution is calculated from the cumulative area at regular intervals of retention time. IBP is defined as the temperature equivalent to the time where first cumulative area is 0.5% of the total. The rest of the boiling point distribution is calculated from the cumulative area at a given time equivalent to the particular temperature and tabulated percentage of sample boiling versus the corresponding temperature.

Hydroprocessing

Hydroprocessing of AR and VR2 resids was performed in the absence and presence of commercial Co-Mo/ Al_2O_3 (Shell 344TL, also called Criterion 344TL) catalyst. Table 11.1 shows the properties of the catalyst. Prior to the catalytic tests, Co-Mo/ Al_2O_3 catalyst was grounded and presulfided. The hydroprocessing was carried out in a 25 mL horizontal tubing bomb reactor loaded with 3 g of resid and 0.3 g of the catalyst under an initial hydrogen pressure of 6.9 MPa for 60 min. The reaction temperature range was 350–450°C with an interval of 25°C. Details of catalyst sulfidation and hydroprocessing procedures are given elsewhere [9–11]. After the reaction, reactor was quenched in a cold water bath; the products were collected in CS_2 . The solid and liquid products were separated by a filtration. The insoluble solid product is referred to as coke. The liquids were analyzed by HT-SimDis GC. The SimDis analysis data were processed and reported according to the cut point ranges classified in Table 11.2 which is based on the classification proposed by Altgelt and Boduszinski [1] except that the FBP is 847°C instead of

Table 11.1. Properties of the Shell 344TL catalyst

Material Type	Co-Mo/Al ₂ O ₃
CoO, wt%	2.9
MoO ₃ , wt%	13.5
Surface area, m ² /g	208
Pore volume, cc/g	0.53
Median pore Diam., Å	110

Table 11.2. Boiling point range of different fractions

Fraction	Atmospheric Equivalent Boiling Point	
	°C	°F
Light Naphtha	IBP-130	IBP-266
Heavy Naphtha	130-220	266-428
Atmospheric Gas Oil	220-340	428-644
Light Gas Oil	340-450	644-842
Heavy Vacuum Gas Oil	450-540	842-1004
Super Heavy Gas Oil	540-847	1004-1557
Nondistillable Residue	> 847	> 1557

700°C. Resid conversion was calculated from the fractions of > 340°C and >540°C boiling point and the liquid yields.

Results and Discussion

HT-SimDis GC method

In order to establish the right conditions for HT-SimDis GC analysis of resids and their products, analysis was performed at different GC conditions. Table 11.3 lists four different GC methods used for the screening analysis. In the first two methods (TP1 and TP2), detector temperature was 350°C, which is low compared with the other two methods. In method TP2 final GC oven temperature was increased and heating rate reduced compared to those in method TP1. Among methods TP3 and TP4, the heating rate in TP3 is lower than that in TP4. Fig. 11.1 and Fig. 11.2 show the high-temperature gas chromatograms of resids AR and VR2, respectively, corresponding to different GC methods. Comparison of Fig. 11.1B (and Fig. 11.2A) with Fig. 11.1A indicates that at low detector temperature and lower final column temperature (TP1) the GC is not sensitive enough to detect the heavy portion of resids of high boiling range. Increasing the final temperature and total time (in method TP2) improved the elution of heavy materials in the resids, but lower detector temperature was still a problem. Hence in third method TP3, we increased detector temperature, from 350 to 435°C. The gas chromatograms using method TP3 (Fig. 11.1C and Fig. 11.2B) show that the high boiling portion of resid is eluted very well resulting in a significant second peak. To see if there is any further improvement in elution of resid from column, we increased heating rate from 10 to 15°C/min and final holding time from 15.5 to 28.8 min in TP4. Comparing Fig. 11.1D, with Fig. 11.1C or comparing Fig. 11.2C with Fig. 11.2B show that increased heating rate reduced the time needed for resid elution. However, at higher heating rate getting reproducible retention times during calibration was a problem because of faster elution of the compounds with low resolution. Based on the results of screening among four

Table 11.3. Different GC methods for HT-SimDis analysis

Method	Detector Temp. (°C)	Column Temperature Program					Total Time (min)
		Initial Temp. (°C)	Initial Time (min)	Rate (°C/min)	Final Temp. (°C)	Final Time (min)	
TP1	350	40	1	15	355	18.0	40
TP2	350	40	1	10	425	15.5	55
TP3	435	40	1	10	425	15.5	55
TP4	435	40	1	15	425	28.8	60

Figure 11.1 HT-SimDis gas chromatograms of AR obtained using GC methods A) TP1, B) TP2, C) TP3 and D) TP4.

Figure 11.1 Cont'd...

Figure 11.2 HT-SimDis gas chromatograms of VR2 obtained using GC methods A) TP1, B) TP2, C) TP3 and D) TP4.

Figure 11.2 Cont'd...

methods given in Table 11.2, TP3 is a good method with respect to detector sensitivity, elution of high molecular weight compounds, reproducibility and the correct calibration. Hence method TP3 was chosen for subsequent GC analysis.

To further confirm the general applicability of the method TP3, it was checked with a reference standard (high-temperature lube oil) and various model compounds. Fig. 11.3 shows the high-temperature gas chromatograms of reference standard, AR and VR2, respectively along with calibration curves. It is clear from Fig. 11.3 that calibration curve is linear except for very light and fast eluting paraffins (C_5 - C_9). For the analysis of resids, it is necessary to calibrate to as high boiling point as possible. In this work it was possible to calibrate through C_{92} paraffin which has a boiling point of 704°C . The reference standard is eluting within the range covered by the calibration curve (Fig. 11.3A). The atmospheric equivalent boiling point (AEBP) distribution obtained for the reference standard using our calibrated HT-SimDis is very close (within $\pm 3\%$) to the values supplied by the vender for that standard. In the case of AR and VR2, a part of their chromatograms is beyond the range of the calibration standard (Fig. 11.3B and 11.3C), but it was assumed that the calibration is linear in all the range of resids elution.

In order to check the HT-SimDis applicability to various compounds, we also analyzed different types of pure compounds and estimated their boiling points using HT-SimDis method. For a pure compound the initial boiling point (where 0.5 wt% sample is distilled) from HT-SimDis was taken as the estimated boiling point of that compound. Table 11.4 lists the estimated boiling points of the compounds. The boiling points derived from SimDis GC are consistent with the true boiling points within $\pm 5\%$ for most compounds, and $\pm 7\%$ for some compounds. It seems that the SimDis GC-derived boiling points tend to be slightly lower for many polycyclic aromatic compounds and polar compounds containing heteroatoms. However, the accuracy is considered to be acceptable for analyzing such complicated mixtures as resids.

Table 11.4. Comparison of HT-SimDis derived boiling points with the true values of various compounds

Compounds	True Boiling Point		SimDis-BP		Deviation	
	°C	°F	°C	°F	°C	% in °C
Cycloalkanes:						
Methylcyclohexane	101	214	104	220	3	3.3
trans-1,3-Dimethylcyclohexane	124	255	133	271	9	7.0
n-Hexylcyclohexane	221	430	223	434	2	1.8
cis-Decalin	193	379	197	387	4	2.3
trans-Decalin	185	365	194	381	9	4.8
Ethylcyclohexane	130	266	128	262	-2	-1.8
n-Propylcyclohexene	155	311	156	313	1	0.6
n-Butylcyclohexane	180	356	179	354	-1	-0.6
Aromatics:						
Toluene	110	230	118	244	8	6.8
p-xylene	139	282	140	283	1	0.4
Ethylbenzene	136	277	143	289	7	4.9
Naphthalene	218	424	218	425	0	0.1
Cyclohexylbenzene	239	462	240	464	1	0.4
2-Methylnaphthalene	241	466	237	459	-4	-1.6
1-Methylnaphthalene	240	464	227	441	-13	-5.2
2,6-Dimethylnaphthalene	262	504	275	527	13	5.0
1,5-Dimethylnaphthalene	266	511	278	532	12	4.4
Fluorene	298	568	291	556	-7	-2.2
Biphenyl	255	491	258	497	3	1.2
p-Terphenyl	389	732	383	721	-6	-1.6
Phenanthrene	336	637	320	607	-16	-4.8
Anthracene	342	648	340	643	-2	-0.7
Pyrene	395	743	382	719	-13	-3.4
Chrysene	447	837	418	784	-29	-6.6
Heteroatom-containing compounds:						
Phenol	182	360	172	341	-10	-5.7
m-Cresol	203	397	197	386	-6	-3.2
2-Naphthol	285	545	284	543	-1	-0.3
Dibenzofuran	285	545	298	569	13	4.6
Quinoline	237	459	227	441	-10	-4.2
1,2,3,4-Tetrahydroquinoline	249	480	247	477	-2	-0.7
Acridine	346	655	349	659	3	0.7
Benzothiophene	221	430	219	426	-2	-0.8
Dibenzothiophene	332	630	317	603	-15	-4.5

Figure 11.3 HT-SimDis gas chromatograms of A) high temperature lube oil (reference standard), B) atmospheric resid (AR) and C) vacuum resid (VR2).

Figure 11.3 Cont'd...

Analysis of resid feedstocks

HT-SimDis gas chromatograms of AR and VR2 resids contain two major peaks (Fig. 11.3B and 11.3C). In the case of VR2 resid the second peak at high temperature region is more intensive compared to AR resid, indicating that the VR2 contains more high boiling fraction. The first peak and the second peak in Fig. 11.3B (AR) correspond to AEBP of about 450°C and 704°C, respectively; the two peaks in Fig. 11.3C (VR2) correspond to AEBP of about 608°C and 704°C, respectively.

Table 11.5 shows the AEBP distribution of AR and VR2 obtained using HT-SimDis, according to the boiling ranges shown in Table 11.2. The fractions with boiling point of >340°C (cut-off point for atmospheric distillation) in AR and VR2 are 93.9 and 99.1 wt%, respectively. The fractions with AEBP of > 540 °C (cut-off point for vacuum distillation) in AR and VR2 are 57.0 and 88.6 wt%, respectively. Table 11.5 also shows the amount of residue (uneluted portion of the sample) estimated by HT-SimDis. The amounts of residue (with AEBP of >847°C) in AR and VR2 feedstocks are 16.5 and 21.6 wt%, respectively. The amounts of asphaltenes for AR and VR2 feeds were estimated from solvent extraction method and the values are 9.22 and 14.02 wt%, respectively. It is interesting to note that these residue values are considerably higher than the asphaltene contents. AR is completely soluble in toluene, and VR2 only contains 0.12 wt% toluene-insoluble material.

Fig. 11.4 and Fig. 11.5 illustrate the high-temperature gas chromatograms of feedstock, hexane soluble (HS) and hexane insoluble (HI) fractions of AR and VR2, respectively. HT-SimDis gas chromatograms of feedstocks and HS fractions of AR (Fig. 11.4) and VR2 (Fig. 11.5) show two peaks, but hexane insoluble (HI) fractions of both AR (Fig. 11.4C) and VR2 (Fig. 11.5C) resids show a single peak at high temperature. Essentially all HI are asphaltenes in these resids. We have found no literature report on HT-SimDis GC of asphaltene. The peak AEBP for asphaltene in AR (Fig 11.4) is 704°C, which correspond to a GC oven temperature of

Table 11.5. HT-SimDis GC analysis of AR and VR2 resid feedstocks

Feed	Atmospheric Equivalent Boiling Point Distribution (%)						Residue ^b
	IBP-220°C	220-340°C	340-450°C	450-540°C	540-700°C	700°C-FBP ^a	
AR	0.5	5.6	17.7	19.2	27.4	13.1	16.5
VR2	0.3	0.6	2.0	8.5	43.1	23.9	21.6

a Final boiling point, FBP: $\leq 847^{\circ}\text{C}$

b Residue : uneluted portion of the resid with AEBP of $>847^{\circ}\text{C}$.

Figure 11.4 HT-SimDis gas chromatograms of A) AR, B) hexane soluble AR and C) hexane insoluble AR.

Figure 11.4 Cont'd...

Figure 11.5 HT-SimDis gas chromatograms of A) VR2, B) hexane soluble VR2 and C) hexane insoluble VR2.

Cont'd...

Figure 11.5 Cont'd...

425°C. The majority of the asphaltene peak eluted between GC retention time of 32-48 min, which correspond to a AEBP range of 620-840°C, and a GC oven temperature of 425°C. A question that arises is, whether this peak truly represent asphaltene or the products of asphaltene decomposition. It is known that decomposition of asphaltene can occur at this temperature range [12]. It is difficult to clarify this issue for asphaltene, because no standard reference is available. However, what we have established is that this peak is characteristic of the presence of very heavy materials, and this peak can disappear after upgrading. The eluted materials in Fig. 11.4C only represent 50.1 wt% of the asphaltene fraction in AR. Similarly, the eluted materials in Fig. 11.5C represent only 39.7 wt% of the HI (mostly asphaltene) in VR2.

Another interesting feature is that the HS fraction of AR, the asphaltene-free materials, also displays the GC peak with AEBP of about 704°C (Fig. 11.4B), which is almost identical to that for asphaltene (Fig. 11.4C). This trend can also be observed for VR2 in Fig. 11.5. Apparently, asphaltene fractions contribute only partially to the second peak of the whole resids. These results show that asphaltene-free resids contain a significant amount of materials which have the same AEBP range as asphaltene. Such elutable heavy materials largely disappear in HT-SimDis GC of the upgrading products, as described below. HT-SimDis gas chromatograms of HI fractions (Fig. 11.4C, Fig. 11.5C) and Table 11.5 clearly show that VR2 feed contains more high boiling fraction (second peak) and more asphaltenes compared to AR feed.

Analysis of upgrading products

Fig. 11.6 and Fig. 11.7 compare the high-temperature gas chromatograms of AR and VR2 feeds and their products obtained over Co-Mo/Al₂O₃ catalyst at 425°C, respectively. Compared to the AR feedstock, the chromatogram of products has more lighter components, and the second GC peak (due to heavy fraction of the feedstocks) eluting at higher temperature (Fig. 11.6) almost disappeared. This trend is more remarkable for VR2 (Fig. 11.7). Complete AEBP distribution of the liquid products, liquid yield, coke yield, and conversions of >340°C and >540°C fractions at

Table 11.6. HT-SimDis GC analysis of hydroprocessed AR resid over Co-Mo/Al₂O₃

Expt. ID	Catalyst	Reaction Temp. (°C)	Atmospheric Equivalent Boiling Point Distribution (%)							Liquid Yield (wt%)	Coke Yield (wt%)	>340°C Conv. (%)	>540°C Conv. (%)
			IBP-220°C	220-340°C	340-450°C	450-540°C	540-700°C	700°C-FBP ^a	Residue ^b				
1	None	375	0.9	6.5	18.6	19.5	28.1	13.4	13.0	97.2	0.1	4.1	0.4
5	None	400	1.0	9.6	20.8	19.3	24.6	10.6	14.1	95.5	0.2	9.1	11.5
7	None	425	12.3	19.1	21.1	13.2	13.7	6.1	14.5	97.7	0.4	28.6	37.0
27	Co-Mo/Al ₂ O ₃	375	0.7	7.0	19.9	20.3	28.2	12.9	11.0	97.2	0.1	4.4	4.8
20	Co-Mo/Al ₂ O ₃	400	1.1	8.1	19.8	19.3	24.9	10.8	16.0	97.6	0.1	5.6	5.2
21	Co-Mo/Al ₂ O ₃	425	5.4	13.7	22.7	18.5	19.9	7.1	12.7	94.8	0.2	18.3	29.3

^a Final boiling point, FBP: ≤ 847°C

^b Residue : uneluted portion of the resid with AEBP of >847°C.

Table 11.7. HT-SimDis GC analysis of hydroprocessed VR2 resid over Co-Mo/Al₂O₃

Expt. ID	Catalyst	Reaction Temp. (°C)	Atmospheric Equivalent Boiling Point Distribution (%)							Liquid Yield (wt%)	Coke Yield (wt%)	>340°C Conv. (%)	>540°C Conv. (%)
			IBP-220°C	220-340°C	340-450°C	450-540°C	540-700°C	700°C-FBP ^a	Residue ^b				
40	None	400	2.4	4.4	7.1	12.8	39.7	18.9	14.7	97.3	0.2	8.5	16.0
31	None	425	6.2	13.0	14.2	13.4	21.3	7.7	24.2	95.2	1.9	22.4	40.3
37	None	450	8.6	27.2	21.5	12.5	13.3	6.0	10.9	77.6	13.6	49.8	72.4
47	Co-Mo/Al ₂ O ₃	350	0.9	3.5	4.4	10.0	42.4	21.4	17.4	97.6	0.1	5.8	6.6
46	Co-Mo/Al ₂ O ₃	375	1.2	3.6	4.4	10.2	40.0	20.4	20.2	97.2	0.1	6.6	7.7
42	Co-Mo/Al ₂ O ₃	400	2.6	5.0	7.0	12.9	39.8	18.1	14.6	97.0	0.2	9.6	17.2
33	Co-Mo/Al ₂ O ₃	425	5.6	10.7	14.3	17.2	29.1	9.5	13.6	94.6	0.4	20.1	41.8
38	Co-Mo/Al ₂ O ₃	450	13.9	22.9	20.6	14.0	15.3	6.1	7.2	85.4	1.5	45.6	71.2

^a Final boiling point, FBP: ≤ 847°C

^b Residue : uneluted portion of the resid with AEBP of >847°C.

Figure 11.6 HT-SimDis gas chromatograms of A) AR feed and B) product obtained over CO-Mo/Al₂O₃(shell 344TL) at 425°C.

Figure 11.7 HT-SimDis gas chromatograms of A) VR2 feed and B) product obtained over CO-Mo/Al₂O₃(shell 344TL) at 425°C.

different conditions are shown in Tables 11.6 and 11.7 for AR and VR2, respectively. We have done several repeated analyses for some samples to examine the reproducibility of the HT-SimDis analysis of upgraded products. Table 11.8 shows the good reproducibility of the AEBP distribution of AR, VR2 and their products from repeated analyses. AEBP distribution from Tables 11.6 and 11.7 reveals that both catalytic and noncatalytic upgrading of AR and VR2 produced lighter fraction but the extent of lighter fraction production varied with the type of feedstock and the temperature. Increasing the reaction temperature increased the conversion of $>340^{\circ}\text{C}$ and $>540^{\circ}\text{C}$ fractions both in the presence and absence of catalyst. However, the presence of catalyst has two positive effects: 1) more heavy materials ($>847^{\circ}\text{C}$ fraction) is converted, and 2) the coke formation is suppressed, particularly in the case of VR2 upgrading. Thermal runs produced higher amounts of coke with lower liquid yield at high temperature of 450°C , which indicate the occurrence of significant retrogressive reactions (condensation) of reactive fragments in the absence of catalyst. In the case of VR2 resid upgrading, more of the $>540^{\circ}\text{C}$ fraction is converted, both in catalytic and noncatalytic runs, compared to those of AR resid. Consequently the fractions between IBP- 220°C and 220 - 340°C increased significantly during the hydroprocessing of VR2 resid at 425 - 450°C .

Fig. 11.8 clearly illustrates that the reaction temperature has a significant influence on product distribution, particularly on $>540^{\circ}\text{C}$ fractions. At lower reaction temperature ($<400^{\circ}\text{C}$) there is no significant change in $>540^{\circ}\text{C}$ fractions. But increase in temperature from 400°C to 425°C led to significant conversion of heavy materials with AEBP of 540 - 700°C range, resulting in increased amounts of lighter fractions ($<450^{\circ}\text{C}$). It indicates that increasing the reaction temperature causes the production of large amounts of lighter fractions ($<540^{\circ}\text{C}$) at the expense of heavier fractions ($>540^{\circ}\text{C}$). When the temperature is further increased to 450°C , the $>540^{\circ}\text{C}$ fractions converted more significantly, however, the fraction with AEBP of 450 - 540°C behaved differently from the run at 425°C . At 425°C , the content of 450 - 540°C fraction is higher than in 450°C run, which indicates that at higher reaction temperature, this fraction is also converted. These results indicate

Table 11.8. Reproducibility check for HT-SimDis GC analysis of AR and VR2 feedstocks and some VR2 products

Expt. ID	Temp. (°C)	Atmospheric Equivalent Boiling Point Distribution (%)						Residue ^b
		IBP-220°C	220-340°C	340-450°C	450-540°C	540-700°C	700°C-FBP ^a	
AR	-	0.5	5.6	17.7	19.2	27.4	13.1	16.5
AR	-	0.6	5.4	17.5	19.2	27.3	13.4	16.6
VR2	-	0.3	0.6	2.0	8.5	43.1	23.9	21.6
VR2	-	0.4	0.6	2.0	8.6	44.4	25.4	18.6
37/A	450	9.2	28.4	22.2	12.4	12.4	4.8	10.6
37/B	450	8.9	27.5	21.9	12.6	13.0	5.3	10.8
37/C	450	8.6	27.5	21.5	12.5	13.3	5.7	10.9
31/A	425	6.7	12.1	13.8	13.4	20.5	8.6	24.9
31/B	425	6.7	11.7	13.6	13.4	20.7	9.4	24.5
31/C	425	6.2	13.0	14.2	13.4	21.3	7.7	24.2
46/A	375	0.7	3.0	4.3	9.9	38.9	18.4	24.8
46/B	375	1.2	3.6	4.4	10.2	40.0	20.4	20.2

a Final boiling point, FBP: $\leq 847^{\circ}\text{C}$

b Residue : uneluted portion of the resid with AEBP of $>847^{\circ}\text{C}$.

Fig. 11.8. Effect of temperature on VR2 hydroprocessing over Co-Mo/Al₂O₃ catalyst.
The residue fraction refers to the uneluted resid products with AEBP of >847°C.

Fig. 11.9 Effect of temperature on sulfur conversion by HDS during VR2 hydroprocessing in the presence and absence of sulfided Co-Mo/Al₂O₃ catalyst.

that in hydroprocessing of VR2, the temperature required to activate >540°C fraction is about 425°C, whereas 450-540°C fraction is activated at about 450°C.

Reduction in boiling points is also accompanied by desulfurization during resid upgrading. Fig. 11.9 demonstrates the effect of temperature on sulfur removal in hydroprocessing of VR2 in the presence and absence of Co-Mo/Al₂O₃ catalyst. Reaction temperature has a significant effect on desulfurization, particularly in the presence of catalyst. Unlike the AEBP distribution, the extent of catalytic desulfurization increased almost monotonically with increase in temperature from 350°C to 450°C. This trend is different from those observed for hydrodesulfurization of distillate fuels, where reaction temperature is typically between 350 ~ 400°C.

It appears that catalytic hydrodesulfurization of resids also depends on thermally-driven hydrocracking reactions. In other words, the C-C bond cleavage reactions are largely thermally driven in the catalytic upgrading. The role of catalyst is twofold: The first is to promote hydrogen transfer to produce stable molecules and suppress coke formation. In the noncatalytic reaction the coke formation is significant at 450°C (Table 11.7). The second is to enhance the desulfurization of relatively smaller molecules derived from the resids.

Conclusions

For simulated distillation of heavy liquids such as heavy petroleum fractions and coal liquids using GC, it is important to use right GC conditions. After screening tests at different GC conditions in this work, a HT-SimDis GC method has been established, which can be used to determine AEBP distribution up to as high as 847°C. It has been successfully applied for analyzing the AEBP distribution of an atmospheric resid (AR) and a vacuum resid (VR2) as well as their products from catalytic hydroprocessing.

HT-SimDis GC analysis of AR and VR2 feedstocks clearly indicated the difference in AEBP distribution between the two feedstocks, which is responsible, at least in part for different level of upgrading. AEBP distribution of hydroprocessed products revealed that both thermal and catalytic hydroprocessing of AR and VR2 strongly depend on the reaction temperature. They produced significant amounts of lighter fractions, and also caused changes in higher boiling fractions (>450°C AEBP). For the runs over a sulfided Co-Mo/Al₂O₃ catalyst, the yields of products with AEBP range of 540-700°C remained almost constant when the reaction temperature was within 350-400°C, but decreased monotonically with further increasing reaction temperature up to 450°C. At high reaction temperature (450°C), the 450-540°C fraction is also converted significantly. The extent of catalytic hydrodesulfurization over Co-Mo/Al₂O₃ catalyst increased monotonically with increase in reaction temperature from 350 to 450°C.

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Appendix 1:

List of Publications Related to This Project

- Parfitt, D.S., C. Song, H.H. Schobert. The Use of Bimetallic Organometallic Compounds as Precursors of Dispersed Catalysts for Coal Liquefaction. Proc. 9th Ann. Internat. Pittsburgh Coal Conf., University of Pittsburgh, Pittsburgh, Oct. 12-16, 1992, pp. 503-508.
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- Song, C., L. Hou, A. K. Saini, P.G. Hatcher, and H. H. Schobert. CPMAS ^{13}C NMR and Pyrolysis-GC-MS Studies of Structure and Liquefaction Reactions of Montana Subbituminous Coal. Fuel Processing Technol., 1993, 34 (3), 249-276.
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