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**Novel Bimetallic Dispersed Catalysts for
Temperature-Programmed Coal Liquefaction**

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ABSTRACT

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 the development of novel bimetallic dispersed catalysts for temperature-programmed liquefaction.

The ultimate goal of the present research is to develop novel catalytic hydroliquefaction process using highly active dispersed catalysts. The primary objective of this research is to develop 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.

Several heterometallic complexes consisting of two transition metals, Mo and Co, and sulfur in a single molecule were synthesized and tested 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.

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.

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., MoS_2) 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 quarterly report 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.

TECHNICAL PROGRESS

BIMETALLIC DISPERSED SULFIDE CATALYSTS FROM THIOCUBANE PRECURSORS FOR TEMPERATURE-PROGRAMMED COAL LIQUEFACTION

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: $Mo_2Co_2S_4(S_2CNEt_2)_2(CH_3CN)_2(CO)_2$ [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 Watcher²⁴ and Halbert et al.²⁵ For comparative examination, the trianionic bimetallic complex, $(PPh_4)_3Co(MoS_4)_2$, was also synthesized based on the procedure of Pan et al.²⁶ This bimetallic sulfide complex contains cobalt bis-tetrathiomolybdate trianion, $Co(MoS_4)_2^{3-}$, 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.

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 Co₂(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 H₂ 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 N₂ 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

Effects of Precursor Type and IWI Solvents

Table I shows the results of catalyst screening for liquefaction of the Montana subbituminous coal at 400 °C for 30 min. We first prepared and tested Mo₂Co₂S₄(S₂CNEt₂)₂(CH₃CN)₂(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 CH₃CN 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 I. 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 Mo₂Co₂S₄Cp₂(CO)₂ [MoCo-TC2], and Mo₂Co₂S₄(Cp')₂(CO)₂ [MoCo-TC3]. Figure 1 shows the structures of the thiocubanes. The basic difference between these three thiocubanes is the type of ligands bound to the Mo [Cp = C₅H₅, Cp' = C₅Me₅; all the five carbon atoms in the cyclopentadiene ring are equidistant from the metal atom].

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, 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 H₂. This pressure-drop is due to the adsorption and dissociation of H₂ gas by the catalyst and subsequent hydrogen transfer to the coal species, as also observed for other dispersed catalyst systems.¹⁸ Table II 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 I and II), 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 I and II. 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 I). 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 II, 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 recharged 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. Figure 3 shows the structure of the Co(MoS₄)₂³⁻ trianion. Preliminary results in Table I and Table II 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 I. 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.

From the data in Tables 1 and 2, 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 $\text{Co}_2\text{Mo}_2\text{S}_4$, the differences in catalytic activity between the three thiocubanes clearly indicate the importance of ligand type (Figure 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 1), while in MoCo-S, the Co and Mo are bound through sulfur-bridge bonding but there are no direct metal-metal bonds (Figure 3). 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 III 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.

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 III. 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 III 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 III. 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 III). 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 III.

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 H_2 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 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 4 indicates that the latter method gave slightly higher conversion. It is clear from Figure 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 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 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 Carbon

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. 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 5 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.

Both the oxide and sulfide of Mo are catalytically active for hydrogenation reactions but the sulfide is superior.¹⁸ When $Mo(CO)_6$ or $Co_2(CO)_8$ 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 5). 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 H_2 - H_2S (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, $Mo(CO)_6 + Co_2(CO)_8 + S$, 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 5.

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 $\text{Mo(CO)}_6 + \text{Co}_2(\text{CO})_8$ 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.

REFERENCES CITED

- (1) Sullivan, R.F.; Frumkin, H.A. Prepr. Pap. - Am. Chem. Soc. Div. Fuel Chem., 1986, 31 (2), 325-339.
- (2) Song, C.; Eser, S.; Schobert, H.H.; Hatcher, P.G. Energy & Fuels, 1993, 7, 234-243.
- (3) Weller, S.W. Review paper presented the 4th Int. Conf. on Chem. Uses of Mo., Golden, Colorado, August 9-12, 1982.
- (4) Derbyshire, F.J.; Catalysis in Coal Liquefaction, IEACR/08, IEA Coal Research, London, 1988, 69 pp.
- (5) Swanson, A.; Prepr. Pap. - Am. Chem. Soc. Div. Fuel Chem., 1992, 37(1), 149-155.
- (6) Yamada, O.; Suzuki, T.; Then, J.; Ando, T.; Watanabe, Y.; Fuel Process. Technol., 1985, 11, 297-311.
- (7) Suzuki, T.; Ando, T.; Watanabe, Y., Energy & Fuels 1987, 1, 299-300.
- (8) Herrick, D. E.; Tierney, J. W.; Wender, I.; Huffamn, G. P.; Huggins, F. E., Energy & Fuels 1990, 4, 231-236,
- (9) Artok, L.; Davis, A.; Mitchell, G.D.; Schobert, H.H., Energy & Fuels, 1993, 7, 67-77.
- (10) Hirschon, A.S.; Wilson, R.B.; Am. Chem. Soc. Sym. Ser., 1991, 461, 273-283.
- (11) Hirschon, A.S.; Wilson, R.B.; Fuel, 1992, 71, 1025-1031.
- (12) Satterfield, C.N.; "Heterogeneous Catalysis in Industrial Practice", McGraw-Hill: New York, 2nd Ed., 1991, 554 pp.
- (13) Bond, G.C., "Heterogeneous Catalysis", Oxford Science Publications, Clarendon Press: Oxford, 1987, Chapter 8, pp. 85-103.
- (14) Chianelli, R.R.; Daage, M.; Halbert, T.R.; Ho, T.C.; Stiefel, E.I., Prepr. Pap. - Am. Chem. Soc. Div. Petrol. Chem., 1990, 35 (2), 227-231.
- (15) Nomura, M.; Miyake, M.; Sakashita, H.; Kikkawa, S., Fuel, 1982, 61, 18-20.
- (16) Garg, D.; Givens, E.N.; Fuel Process. Technol., 1984, 8, 123-134.
- (17) Song, C.; Nomura, M.; Miyake, M.; Fuel, 1986, 65, 922-926..
- (18) Song, C.; Nomura, M.; Ono, T., Prepr. Pap. - Am. Chem. Soc. Div. Fuel Chem., 1991, 36(2), 586-596.

- (19) Sommerfeld, D.A.; Jaturapitpornsakul, J.; Anderson, L.; Eyring, E.M.; Prepr. Pap. - Am. Chem. Soc. Div. Fuel Chem., 1992, 37(2), 749-755.
- (20) Mingos, D.M.P.; Wales, D.J., "Introduction to Cluster Chemistry", Prentice Hall: Englewood Cliffs, New Jersey, 1990, 318 pp.
- (21) a) Song, C.; Schobert, H. H.; Hatcher, P. G., Energy & Fuels, 1992, 6, 326-328; b) Song, C.; Schobert, H. H.; Prepr. Pap. - Am. Chem. Soc. Div. Fuel Chem., 1992, 37(2), 976-983.
- (22) Huang, L.; Song, C.; Schobert, H. H., Prepr. Pap. - Am. Chem. Soc. Div. Fuel Chem., 1992, 37(1), 223-227.
- (23) Song, C.; Parfitt, D.S.; Schobert, H. H.; Catal. Lett., 1993, in press.
- (24) Brunner, H.; Wachter, J., J. Organomet. Chem. 1982, 240, C41-44.
- (25) Halbert, T. R.; Cohen, S. A.; Stieffel, E. I., Organometallics 1985, 4, 1689-1690.
- (26) Pan, W.; Johnston, D.C.; McKenna, S.T.; Chianelli, R.R.; Halbert, T.R.; Hutchings, L.L.; Stiefel, E.I., Inorganica Chimica Acta, 1985, 97, L17-L19.
- (27) Solar, J.M.; Derbyshire, F.J.; de Beer, V.H.J.; Radovic, L.R.; J. Catal., 1991, 129, 330-342.
- (28) Halbert, T.R.; Ho, T. C.; Stieffel, E. I.; Chianelli, R. R.; Daage, M., J. Catal. 1991, 130, 116-119.
- (29) Rincon, J.M.; Cruz, S. Fuel, 1988, 67, 1162-1163.
- (30) Song, C.; Hanaoka, K.; Nomura, M.; Fuel, 1989, 68, 287-292.
- (31) Joseph, J.T., Fuel, 1991, 70, 139-144; 459-464.
- (32) Song, C.; Parfitt, D.S.; Schobert, H. H.; Prepr. Pap. - Am. Chem. Soc. Div. Fuel Chem., 1993, 38(2), 546-553.

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

Catalyst precursor	Solvent for catalyst loading ^a	Reaction type	Conversion	Products (wt%, dmmf)		
			dmmf wt%	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 II. 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 III 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.

Figure 1. Structures of three MoCo bimetallic thiocubane clusters [MoCo-TC1: Mo₂Co₂S₄(S₂CNEt₂)₂(CH₃CN)₂(CO)₂; MoCo-TC2: Mo₂Co₂S₄Cp₂(CO)₂; MoCo-TC3: Mo₂Co₂S₄(Cp')₂(CO)₂]. Cp = cyclopentadiene; Cp' = pentamethylcyclopentadiene.

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

Figure 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 5. 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.

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