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Novel Bimetallic Dispersed Catalysts for Temperature-Programmed Coal Liquefaction

**Technical Progress Report
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(Approved)

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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 can be 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.

The primary objective of this research is to explore the potential of bimetallic dispersed catalysts from heterometallic molecular precursors in their use in model compound liquefaction reactions. This quarterly report describes the use of three precursors in model compound reactions. The first catalyst is a heterometallic complex consisting of two transition metals, Mo and Ni, and sulfur in a single molecule. The second is a thiocubane type complex consisting of cobalt, molybdenum and sulfur. The third is a thiocubane type cluster consisting of iron and sulfur 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 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-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.

INTRODUCTION

Dwindling crude oil resources as feedstock for the chemical industry and for transportation fuel compel us to search for alternate sources. Coal¹, consisting of high molecular weight interconnected molecules via alkyl bridges and various functional groups like OH, CO, CO₂H, NH₂, CN, SH and S, provides the necessary material for further exploitation. Coal hydroliquefaction is the method of choice and has its roots in the work of Friedrich Bergius². Coal accounts currently as one of the main US energy sources³. The world's known coal reserves are double the known petroleum reserves. It becomes increasingly important to find an alternative feedstock for the crude oil based fuel- and chemical industry⁴. Coal liquefaction is an important process for producing transportation fuels, useful aromatic chemicals and advanced materials from coal⁵. Despite enormous efforts to reduce the cost of coal-derived distillates, coal-derived products are still not competitive with crude oil products. Typical reaction conditions in coal liquefaction involve the reactions of coal with H₂ in a solvent at high temperature and high pressure. The liquefaction process is extremely intricate and involves both chemical and physical transformations. 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 products depend on the coal, catalyst, solvent and process conditions used in the first stage. The conversion of primary liquefaction products requires upgrading of heavy materials to distillate materials, followed by refining for use as transportation fuels including gasoline, jet fuels, and diesel fuels.

Liquefaction, gasification and pyrolysis products of coal have high contents of polycyclic aromatic compounds. These liquids require catalytic hydroprocessing before they can be used as clean transportation fuels. It has been shown⁶ that catalyst precursors for upgrading coal liquids contained the metal combinations Ni-Mo and Co-Mo. Their use in the petroleum industry is widespread. It has been recognized⁷ that dispersed catalysts can be superior to supported catalysts. Dispersed catalysts offer the advantage of an intimate contact with the surface of coal particles. Most MoS₂-containing catalysts are insoluble in common solvents. Therefore one strategy to increase the dispersion with coal particles lies in preparing soluble precursors which can be transformed into an active catalyst at elevated temperatures.

The classical coal liquefaction process breaks down the macromolecular coal molecules into smaller primary liquefaction products. These products consist mostly of polycyclic aromatic compounds, which need to be further processed for use as transportation fuel, or as a source for chemical upgrading. Coal liquefaction is an intricate process in which complex compounds undergo different type of reactions. Depending on the sort of catalyst, major reaction paths are bond cleavage of larger molecules, hydrogenation, and the reaction of heteroatoms like oxygen, sulfur and nitrogen with active catalyst sites. The complex structure of coal makes it very difficult to determine specific steps in the process of coal liquefaction. Our approach to understand the nature of coal liquefaction was to study a simplified model of coal. The complex molecular structure of coal consists mainly of interconnected polyaromatic hydrocarbons. Our model compound phenanthrene enabled us to focus on its particular structure and bonding pattern to quantitatively study its reactivity towards transition-metal-containing catalysts.

The primary objective of this research is to make novel bimetallic catalysts from organometallic precursors, that can be used in low concentrations but exhibit high activity for efficient conversion of our model compound phenanthrene. 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 catalysts. Homometallic "thiocubane" clusters containing an $M_4(\mu_3-S)_4$ core have been known for some time⁸. MoS_2 -based heterometallic catalysts⁹ have led to the preparation of several heterometallic thiocubanes. However, some novel Lewis acidic Ni and Mo catalysts also enhance coal pyrolysis at moderate (300 °C) temperatures¹⁰. Recent work at Penn State has demonstrated the potential of using dispersed Mo and Fe catalysts¹¹. Especially, hydrotreating reagents such as Co-Mo and Ni-Mo are most promising catalysts. Several reports have demonstrated the synergistic effects for acidic Zn-, Ni-, and Mo and Fe-Mo¹²-based catalysts for coal liquefaction model reactions. Even under severe reaction conditions (440 °C, 2000 psi H_2), significantly higher yields of converted products were observed. The beneficial catalytic effect of multi-component catalytic precursors will be used in our synthesis of a series of organometallic compounds. We can anticipate 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 spontaneous assembly. Advances in homometallic transition-metal sulfide chemistry have led to smaller clusters which are fragments of the thiocubane unit. Heteronuclear thiocubane clusters like $Cp_2M_2S_4$ and $M_2M'_2(\mu_3-S)_4$ have been realized. A virtue of this type of compounds is the availability of a wide variety of $M_2S_4^{2+}$ core compounds having sulphur. This flexibility of different ligands provides structural and electronic variations which are not present in the standard

catalyst $(\text{NH}_4)_2\text{MoS}_4$ (ATTM). To gain a better understanding of the catalytic functions, the model reactions that are to be undertaken using thiocubane and inorganic complexes that contain Fe, Ni, Co, Mo and sulphur either in one molecule or various combinations. The main question that arose from coal liquefaction research is what are the key functions of the catalyst leading to high oil yields and coal conversions. This present research is a fundamental study on catalytic model compound of bimetallic molecular precursors.

Numerous studies have been conducted to find out more about the nature of the decomposition process of catalyst precursors¹³. The microstructure of a given catalyst has a decisive influence on its converting capabilities. Our only way to predetermine the appearance of the catalyst's surface is the choice of the catalyst precursor and under which physical and chemical circumstances it can be thermally decomposed. Important factors are the catalyst formula (ratio transition metals/sulfur), functional groups, electronic structure (e.g. unpaired electrons) and the sort of bonding in the precursor molecule (metal-metal bonds). Even though detailed and exact models about active catalyst sites are missing, it turned out that heterometallic phases containing Mo, Co and sulfur are superior to homometallic phases such as Co_9S_8 and MoS_2 . With this in mind, it is apparent that a primary goal of catalyst precursor synthesis should be the search for methods that generate highly dispersed heterometallic sulfide phases. Two approaches towards highly dispersed heterometallic sulfide phases are imaginable. Method one requires thermal decomposition of molecules in which one, two or more metals are part of the sulfur-ligated cluster. Method two employs chemical alteration of existing MoS_2 -particles with Co-containing chemical reagents. The latter method is hard to realize. Not enough information is available about the structure of reactive edge sites of MoS_2 particles to apply selective chemical reactions. Hence our approach lies in the preparation of organometallic precursors which then will be thermally transformed into active catalyst particles.

TECHNICAL PROGRESS

1. A Brief Literature Survey of Liquefaction Catalysis

Multi-component organometallic precursors, for the catalytic liquefaction of coal, have been researched very little and have yet to be shown whether they will aspire to the technical (and economical) requirements of the petrochemical research community.

Combinations of transition metals, such as Co, Ni, Mo, W and Fe, have been used, in the form of supported catalysts, for the upgrading of coal liquids (Derbyshire, 1989). These metals with the addition of promoter compounds are distributed over a porous support of alumina, or silica-alumina, and then sulphided to achieve an active form. Although very successful in the petroleum refining industry for the conversion of coal liquids to light oils and gases, in the presence of heavier products these catalysts become deactivated, after a number of hours, by deposition on the catalytic surface, loss of active metals and sintering of the catalyst-support system. This deposition is thought to be due to the adsorption and reaction of polycondensed aromatics and heteroatom-containing compounds on the active sites.

Liquefaction of coal to light oils and gases has been shown to be a process involving two stages, each requiring a different set of catalytic properties (Derbyshire et al., 1986): first, the conversion of coal to liquid products and second, the upgrading of these products to light oils. Dissolution catalysts, in numerous forms, have demonstrated the ability to perform both of these functions, with varying degrees of success. Research in the field of dissolution catalysis has centered on the activity and selectivity of two catalyst types, metal sulphides and acid catalysts.

Metal sulphides are hydrogenation catalysts, whose activity is a function of their dispersion and the stoichiometry of their sulphide phase. They are produced in situ from a water- (or oil-) soluble precursor in the presence of a sulphur source and coal (or a coal-solvent slurry). Promotion of hydrogenation by these catalysts can induce bond cleavage and stabilize radicals; thus, MoS₂ has demonstrated hydrogenation, hydrodesulphurization and hydrocracking ability (Derbyshire et al., 1990). Although less effective under the same conditions, an equivalent Fe catalyst played a possible role in the breaking and stabilization of O-containing crosslinks.

Transition metal sulphides, dispersed from many different precursors, have exhibited a preference for specific reaction pathways within the coal liquefaction system. Ni, from a nickel sulphate precursor, in loadings of ~1.5wt% removed 50% organic sulphur from coal, compared with 20% removal for Mo and W loadings of ~3wt% (Garcia et al., 1991). Ni, from a nickel acetate precursor, gave a 96% conversion of phenols (with a 50% total removal of O-containing species) due to the hydrocracking of ether linkages in the coal and the subsequent hydrogenation of the aromatic ring system (Takemura et al., 1988).

As stated above, the second type of dissolution catalysts are the acid catalysts, i.e., metal halides. These promote cleavage (cracking) of the coal molecule. Metal halides have low melting points and significant vapour pressures at subpyrolysis temperatures, giving them better dispersion

and penetration of the coal particle. They are strong acids; therefore, the reaction rate is accelerated and the temperature may be reduced. However, they are costly, corrosive and generally do not promote hydrogenation, so, once cracked, the molecules condense to form high molecular weight materials.

Another type of dissolution catalyst exists. These are transition metals bonded to organic-type ligands (naphthenates and carbonyls). Molybdenum naphthenate has been shown to be highly selective for hydrogenation and hydrodenitrogenation (Curtis et al., 1989), making it a very active catalyst for hydrocarbon production and O- and N- removal. Studies have also indicated its use as a desulphurization catalyst in the conversion of benzothiophene to ethylbenzene (90% conversion) with no intermediate styrene production (Ng et al., 1991).

These differences between metal sulphide, halide and carbonyl compounds are apparent in the reactions of FeCl_3 , FeSO_4 and $\text{Fe}(\text{CO})_5$. A coal conversion of 93%, with 50% being light oils and gases, was obtained using the metal halide, 88% conversion, with 54% light oils and gases, using the sulphide and ~100% conversion, with 57% light oils and gases, using the carbonyl (Watanabe et al., 1984). It was made apparent that a mixture of metal acid with a hydrogenation catalyst would be beneficial (Derbyshire, 1989). Therefore, the target in primary liquefaction, using multi-component catalysts, is to obtain a higher percentage of light oils compared to preasphaltenes, asphaltenes and gases, with a lower hydrogen consumption and using less severe conditions (Song et al., 1991).

Several combinations of multi-component dissolution catalysts have been studied and synergistic effects have been reported (Derbyshire, 1989, 1990).

In the area of coal-oil coprocessing (20% coal and 80% oil) sulphated metal oxides, such as $\text{Mo-Fe}_2\text{O}_3\cdot\text{SO}_4$, were found to be highly active and selective (Pradhan et al., 1991). The sulphate helps to prevent sintering of the oxide, whilst the acid strength of the Fe_2O_3 reduces the particle size (30-100Å) making the catalyst highly dispersive. Mo (and/or Sn) are present for their hydrogenation function at loadings of 0.5-2wt%.

Addition of an alkali metal to ZnCl_2 resulted in an increase in oil yields, a decrease in gas yields and a reduction in hydrogen consumption (Song et al., 1991). Similarly, $\text{NiCl}_2\text{-LiCl-NaCl-KCl}$ (and its molybdenum equivalent) gave high oil yields and lower heteroatom content. The hydrocracking ability of this catalyst was lower than MoCl_2 or ZnCl_2 and showed lower hydrogenation than Ni-MoS_2 . This suppression of the acidity of the metal halide allows

hydrogenation as well as cracking to aid the production of oils and restrict the formation of gaseous products.

Further enhancement of hydrodesulphurization activity by the addition of a transition metal to a binary sulphide was reported (Chiannelli et al., 1990). The precursors in this study were: $\text{Fe}(\text{MoS}_4)_2^{3-}$, the Co equivalent and $\text{Co}_2\text{Mo}_2\text{S}_4$ thiocubane. Of these three precursors, the thiocubane was found to be most active; this may be due to the lower decomposition temperature of the organometallic precursor (Song et al., TPR1). Mo-Co thiocubane gave a 92% conversion, with 46% oil and gas, this was a greater conversion than that achieved by the combination of $\text{Mo}(\text{CO})_6$, $\text{Co}_2(\text{CO})_8$ and sulphur, again showing the synergistic effects of multi-component catalysts (Song et al., 1993, 1994).

From the above review, it may be inferred that a dissolution catalyst containing a combination of transition metals, possibly Mo and Fe in a single organometallic molecule in the presence of a sulphur source, may be favourable for the liquefaction of coal and its subsequent upgrading to oils. Whilst the organometallic molecule provides good dispersion at low loading levels, the Fe and Mo metals (present as sulphides) will promote the cracking of heteroatom linkages and hydrogenation, hydrodesulphurization and hydrocracking respectively.

Although an increase in selectivity has been observed for bimetallic catalysts, no significant increase in these properties has been reported using organometallic precursors for the catalytic liquefaction of coal. However, similar results have been reported, using organometallic precursors, at much lower loading levels of the transition metals than those present in bimetallic catalysts dispersed from other precursors.

References Cited

- Chiannelli, R.R.; Daage, M.; Halbert, T.R.; Ho, T.C.; Stiefel, E.I., Am. Chem. Soc. Div. Petrol. Chem. Prepr., 1990, 35(2), 227.
- Curtis, C.W.; Pellegrino, J.L., Energy and Fuels, 1989, 3, 160.
- Derbyshire, F.J.; Davis, A.; Epstein, M.; Stansberry, P., Fuel, 1986, 65, 1233.
- Derbyshire, F.J., Energy and Fuels, 1989, 3, 273.
- Derbyshire, F.J.; Davis, A.; Schobert, H.H.; Stansberry, P., Am. Chem. Soc. Div. Fuel Chem.

- Prepr., 1990, 35, 51.
- Garcia, A.B.; Schobert, H.H., *Coal Preparation*, 1991, 9, 185.
- Ng, F.T.T.; Walker, G.R., *Can. J. Chem. Eng.*, 1991, 69, 844.
- Pradhan, V.; Tierney, J.W.; Wender, I., *Am. Chem. Soc. Div. Fuel Chem. Prepr.*, 1991, 36(2), 597.
- Song, C.; Nomura, M.; Ono, T., *Am. Chem. Soc. Div. Fuel Chem. Prepr.*, 1991, 36(2), 586.
- Song, C.; Schobert, H.H., D.O.E., "Novel Bimetallic Dispersed Catalysts for Temperature-Programmed Coal Liquefaction.", DE-AC22-92PC92122-TPR-1, Oct-Dec 1992.
- Song, C.; Parfitt, D.S.; Schobert, H.H., *Catalyst Letters*, 1993, 21, 27-34.
- Song, C.; Parfitt, D.S.; Schobert, H.H., *Energy and Fuels*, 1994, 8(2), 313-319.
- Takemura, Y.; Okado, K., *Fuel*, 1988, 67, 1548.
- Watanabe, Y.; Yamada, O.; Fujita, K.; Takegami, Y.; Suzuki, T., *Fuel*, 1984, 63, 752.

2. Phenanthrene Hydrogenation over Bimetallic Catalysts

EXPERIMENTAL PART

We focused our experimental work in this quarter on the studies of phenanthrene as a model compound for coal hydroliquefaction reactions in the presence of solvent and bimetallic catalyst precursors. Also, experiments without solvent and catalysts were carried out to get comparable data.

Liquefaction 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.

ATTM was purchased from the vendor Aldrich and was used as obtained, without further purification. The organometallic compounds used in the model compound conversion reactions contain different transition metals and sulfur in the same molecule. The compound with the combination Co-Mo was available in our group and prepared by Dr. Derrick S. Parfitt (now working at PETC). The complexes $[(C_6H_5)_4P]_2[Ni(MoS_4)_2]^{14}$ (Ni-Mo) and $[C_5H_5FeS_4]_4^{15}$ (Fe₄) were prepared according to the methods described in the literature. 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. The structure can be described as two-dimensional chains where the transition metals are surrounded by sulfur in a tetrahedral environment. Müller et al. 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.

Results and Discussion

Catalyst-free model compound liquefaction

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 %.

Catalyst controlled model compound liquefaction

Tables 1-4 show the result of the hydrogenation of phenanthrene in dependence of the catalyst concentration. 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.

Temperature controlled model compound liquefaction

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 and 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 radicals¹⁶.

Model compound studies

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 unsym-octahydrophenanthrene (sym-OHP and unsym-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.

Literature cited

- (1) Larsen, J.W.; Green, T.K., and Kovac, J.J., *J. Org. Chem.*, 1985, 50, 4729.
- (2) A godd review about the roots of Conversion of Coal is given in: Stranges, A.N., *Fuel Processing Technology*, 16 (1987): 205-255.
- (3) Lepkowski, W.; and Nozaki, M., *Chem. Eng. News*, June 17:20-31.
- (4) Speight, J.G. (Ed.), *The Chemistry and Technology of Petroleum*. Marcel Dekker, New York, 760.
Sheldon, R.A., 1983. *Chemicals from Synthesis Gas*. Reidel, Boston, MA.
- (5) Murakami, H., 1987. *Nenryo Kyokai-Shi*, 66 (6): 448-458.
Mikami, K., *Aromatics*, 40 (1-2): 26-29.
Collin, G., *Erdöl u. Kohle-Erdgas Petrochem.*, 38 (11): 489-496.
Kikuchi, E.; Ariyoshi, J.; Sugi, Y.; Horida, Z.; and Iwasaki, M., 1989. *Petrotech*, 12 (2): 78-85.
- (6) Massoth, F.E., *Adv. Catal.* 1978, 27, 265.
Jacobson, A.C., in "Surface Properties and Catalysis by Non-Metals" (Edited by Bonelle, J.P. et al.) 1983, 305-317, Reidel, Dordrecht.
- (7) Hirschon, A.S., and Wilson, R.B., *Am. Chem. Soc. Sym. Ser.*, 1991, 461, 273-283.
- (8) Eltzner, W.; Breysse, M.; Lacroix, M.; and Vrinat, M., *Polyhedron*, 5, 1986, 203.
Eltzner, W.; Breysse, M.; Lacroix, M.; Leclercq, C.; Vrinat, M.; Müller, A.; and Diemann, E., *Polyhedron*, 7, 1988, 2405.
- (9) Gates, B.C.; Katzer, J.R.; Schuit, G.C.A. "Chemistry of Catalytic Processes"; McGraw-Hill: New York, 1979, 390-445.
- (10) Song, C.; Nomura, M.; Miyake, M.; *Fuel*, 1986, 65, 922-926.
Song, C.; Nomura, M.; Ono, T., *Prepr. Pap.-Am. Chem. Soc. Div. Fuel Chem.*, 1991, 36(2), 586-596.
- (11) Artok, L.; Davis, A.; Mitchell, G.D.; Schobert, H.H., *Energy & Fuels*, 1993, 7, 67-77.
- (12) Garg,D.; Givens, E.N.; *Fuel Process. Technol.*, 1984, 8, 123-134.
- (13) Halbert, T.R.; Ho, T.C.; Stiefel, E.I.; Chianelli, R.R.; and Daage, M., *Journal of Catalysis*, 130, 1991, 116-129.
Pan, W.H.; McKenna, S.T.; Chianelli, R.R.; Halbert, T.R.; Hutchings, H.H.; and Stiefel, E.I., *Inorg. Chim. Acta*, 97, L17 (1985).
Stiefel, E.I.; Pan, W.H.; Chianelli, R.R.; and Ho, T.C., U.S. Patent No. 4.581.125 (1986).

- Curtis, M.D.; Penner-Hahn, J.E.; Schwank, J.; Barralt, O.; McCabe, D.J.; Thompson, L.; and Waldo, G., *Polyhedron*, 1, 1988, 2411.
- (14) Müller, A.; Ahlborn, E.; Heinsen, H.-H., *Z. anorg. allg. Chem.* 386, 1971, 102-106.
- (15) Schunn, R.A.; Fritchie, C.J.; and Prewitt, C.T., *Inorganic Chemistry*, 1966, 892-899.
- (16) Song, C.; Hanaoka, K., and Nomura, M., *Fuel*, 1989, 68, 287.
Song, C.; Ono, T., and Nomura, M., *Bull. Chem. Soc. Japan*, 1989, 62, 630-632.
- (17) Song, C.; Hanaoka, K.; Ono, T., and Nomura, M., *Bull. Chem. Soc. Japan* 1988, 61, 3788.
- (18) Song, C.; Parfitt, D.P., and Schobert, H.H., *Am. Chem. Soc. Div, Fuel Chem. Prepr.*, 1993, 38 (2), 546-553.
- (19) Curtis, W.C., and Pellegrino, J.L., *Energy and Fuels*, 1989, 3, 160-168.
- (20) Schiller, G.; in: *Houben-Weyl. Vol. IV/2*, 1955, 248-303.
Wimmer, K., in: *Houben-Weyl VolIV/2*, 1955, 143-152, 163-192.

Table 1: Model compound liquefaction reactions

Catalyst Metal concentration	ATTM 0.37 wt % Mo	None	ATTM 0.37 wt % Mo	ATTM 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 [%]			1.1	6.4
sym-OHP [%]			0.9	0.8
cis-unsym-OHP [%]			1.0	2.0
trans-unsym-OHP [%]				
Total conversion [%]	0.0	7.2	38.1	36.9

Table 2: Model compound liquefaction reactions

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 3: Model compound liquefaction reactions

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: Model compound liquefaction reactions

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 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

Scheme VI

**STRUCTURE OF THE BIMETALLIC THIOCUBANE
Co-Mo**

Scheme VII

SYNTHESIS OF THE CATALYST PRECURSOR

Thiocubane type

Scheme VIII

DATE

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