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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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TABLE OF CONTENTS

Abstract	1
Introduction	2
Structural details of the organometallic catalyst precursor	3
Experimental Part	4
Background information about synthesis of catalyst precursors	4
Synthesis of $[(C_6H_5)_4P]_2[Ni(MoS_4)_2]$, Ni-Mo	5
Synthesis of $[(C_5H_5)FeS]_4$, Fe₄	6
Literatur cited	8
Schemes	

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 novel bimetallic dispersed catalysts from heterometallic molecular precursors, that can be used in low concentrations but exhibit high activity for efficient hydrol liquefaction of coals under temperature-programmed conditions. This quarterly report describes the preparation of two precursors. The first is a heterometallic complex consisting of two transition metals, Mo and Ni, and sulfur in a single molecule synthesized. The second is a thiocubane type cluster consisting of iron and sulfur.

INTRODUCTION

Coal accounts currently as one of the main US energy sources¹. World's known coal reserves are double the known petroleum reserves. It is important to develop alternative feedstocks for the chemical industry². Coal liquefaction is an important process for producing transportation fuels, useful aromatic chemicals and advanced materials from coal³.

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 reducing (H_2) 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 shown that catalysts precursors for upgrading coal liquids contained the metal combinations Ni-Mo and Co-Mo. They have wide spread applications in industry. It has been recognized that dispersed catalysts can be superior to supported catalysts for coal liquefaction. Dispersed catalysts offer the advantage of an intimate contact with the surface of coal particles. Most catalysts are insoluble in common solvents. Therefore one strategy to increase the dispersion on coal particles lies in preparing soluble precursors which can be transformed into an active catalyst at elevated temperatures. Homometallic "thiocubane" clusters containing an $M_4(\mu_3-S)_4$ core have been known for some time. MoS_2 -based heterometallic catalysts⁴ 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) temperatures⁵. Recent work at Penn State has demonstrated the potential of using dispersed Mo and Fe catalysts⁶. Especially hydrotreating reagents such as Co-Mo and Ni-Mo are most widely-used catalysts. Several reports have demonstrated the synergistic effects for acidic Zn-, Ni-, and Mo and Fe-Mo⁷-based catalysts for coal liquefaction model reactions. Even under severe reaction conditions (440 °C, 2000 psi

H₂), 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 multicomponent catalysts could lead to improved catalytic activity for primary coal liquefaction products. 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 Cp₂M₂S₄ and M₂M₂'(μ₃-S)₄ have been realized. A virtue of this type of compounds is the availability of a wide variety of M₂S₄²⁺ core compounds having sulphur. This flexibility of different ligands provides structural and electronic variations which is not present in the standard catalyst precursors (ATM) (NH₄)₂MoS₄. To gain a better understanding of the catalytic functions, the model reactions will be carried out using thiocubane and inorganic complexes that contain Fe, Ni, Co, Mo and sulphur in either one molecule or various combinations. The main question that arises from coal liquefaction research is what are the key functions of the catalyst leading to high oil yields and coal conversions. The present research is a fundamental study on catalytic model compound reactions using bimetallic molecular precursors.

Numerous studies have been conducted to find out more about the nature of the decomposition process of catalyst precursors⁸. Even though detailed and exact models about active catalyst sites are not available, it appears that heterometallic phases containing Mo, Co and sulfur are superior to homometallic phases such as Co₉S₈ and MoS₂. 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 MoS₂-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 MoS₂ 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.

Structural details of the organometallic catalyst precursors

The microstructure of a given catalyst has a decisive influence on its converting capabilities.

Our only way to predetermine the appearance of the catalysts 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).

This report will give detailed information regarding the synthesis and structure of the catalyst precursor molecule $[\text{C}_5\text{H}_5\text{FeS}_4]$.

The functional groups, as shown in scheme IV $[\text{C}_5\text{H}_5\text{FeS}_4]$ ⁹, 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 bond¹⁰. 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 ferrocene¹¹, but agrees very well that of 1.75 Å found in $[(\text{Cp})\text{Fe}(\text{CO})_2]_2$ ¹². Other tetrahedral complexes¹³ are known and also based on transition-metal ligand cubic structures.

EXPERIMENTAL PART

Background information about synthesis of catalyst precursors

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 prepared by Dr. Derrick S. Parfitt (who is now working at Pittsburgh

Energy Technology Center). 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 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 tetrahedral environment. Müller et al.¹⁴ 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.

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 Wachter¹⁶.

Synthesis of $[(C_6H_5)_4P]_2[Ni(MoS_4)_2]$, Ni-Mo

Experimental

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 the supplier "Aldrich". Nickel(II)chloride was found to be available in group resources (obtained earlier from Strem). The reaction pathway leading to the product is described under Scheme II and Scheme III reflects the reported structure.

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 $\cdot 6\text{H}_2\text{O}$ (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).

Observations

The diamagnetic product is like its analogues $[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{M}(\text{MoS}_4)_2]$ ($\text{M} = \text{Fe}, \text{Ni}, \text{Zn}$) 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 $[(\text{C}_5\text{H}_5)\text{FeS}]_4$, Fe₄

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 the vendor "Aldrich" and used without prior purification. Scheme V shows the equation leading to the catalyst precursor.

About 500 mL toluene were placed in a 1 l flask, sulfur (S₈) (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 [(C₅H₅)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.

Observations

[(C₅H₅)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.

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Scheme I

Organometallic Catalyst Precursors

Abbreviation	Molecular Formula	Structure type
Ni-Mo	$[(C_6H_5)_4P]_2[Ni(MoS_4)_2]$	Sulfide complex ^a
Fe ₄	$[(C_5H_5)FeS]_4$	Thiocubane ^b

a) Mueller, A.; Ahlborn, E.; Heinsen, H.-H., Z. anorg. allg. Chem. 386, 1971, 102-106.

b) Schunn, R.A.; Fritchie, C.J.; and Prewitt, C.T., Inorganic Chemistry, 1966, 892-899.

Scheme II

SYNTHESIS OF THE BIMETALLIC SULFIDE $[(\text{C}_6\text{H}_5)_4\text{P}]_2[\text{Ni}(\text{MoS}_4)_2]$

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 TETRAMETALLIC
CATALYST
PRECURSOR $[(C_5H_5)FeS]_4$
Thiocubane type**

Scheme V

SYNTHESIS OF THE CATALYST PRECURSORS

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