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NEW CATALYSTS FOR COAL LIQUEFACTION AND NEW NANOCRYSTALLINE CATALYSTS SYNTHESIS METHODS

J. C. Linehan
D. W. Matson
J. G. Darab

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Pacific Northwest Laboratory
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PI (Authors): John C. Linehan (PI), Dean W. Matson, and John G. Darab

INSTITUTION: Pacific Northwest Laboratory[1]

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PROJECT OBJECTIVE: *To develop highly active nanocrystalline iron-based coal liquefaction catalysts using novel synthetic methods.*

Introduction

The use of coal as a source of transportation fuel is currently economically unfavorable due to an abundant world petroleum supply and the relatively high cost of coal liquefaction. A current estimate for the cost of converting coal to an equivalent of petroleum crude is greater than $30/bbl while the cost of the petroleum is less than $20/bbl.[2] Consequently, a reduction in the cost of coal liquefaction, for example by using less and/or less costly catalysts or lower liquefaction temperatures, must be accomplished if coal is to play an significant role as a source of liquid feedstock for the petrochemical industry. We and others have investigated the applicability of using inexpensive iron-based catalysts in place of more costly and environmentally hazardous metal catalysts for direct coal liquefaction.[3]

Iron-based catalysts can be effective in liquefying coal and in promoting carbon-carbon bond cleavage in model compounds.[3] We have been involved in an ongoing effort to develop and optimize iron-based powders for use in coal liquefaction and related petrochemical applications. Our research efforts in this area have been directed at three general areas. We have explored ways to optimize the effectiveness of catalyst precursor species through use of nanocrystalline materials and/or finely divided powders. In this effort we have developed two new nanophase material production techniques, Modified Reverse Micelle (MRM) and the Rapid Thermal Decomposition of precursors in Solution (RTDS). A second effort has been aimed at optimizing the effectiveness of catalysts by variations in other factors. To this we have investigated the effect that the crystalline phase has on the capacity of iron-based oxide and oxyhydroxide powders to be effectively converted to an active catalyst phase under liquefaction conditions. And finally, we have developed methods to produce active catalyst precursor powders in quantities sufficient for pilot-scale testing. Major results in these three areas are summarized below.

Catalyst Synthesis

The benefits of using ultrafine powders for heterogeneous catalysis applications are well established (e.g., large exposed surface per gram of catalyst, high dispersibility, etc.). However, most synthesis methods for producing "nanocrystalline" catalyst materials involve low production capacity, even on a laboratory scale. We have taken two distinct approaches in our efforts to develop high capacity synthesis methods for active nanocrystalline powders suitable for direct coal liquefaction.

Modified Reverse Micelles. Reverse micelle systems, also called water-in-oil microemulsions, consist of discreet water droplets surrounded by surfactant shells and dispersed in a continuous organic phase. If the droplets are sufficiently large (≥1 nm in diameter), they act as bulk water and conventional aqueous chemistry can be performed within their cores. Consequently, the individual micelles can be viewed as submicroscopic reaction vessels suitable for particle synthesis by conventional precipitation methods. In addition, because nucleation occurs in the presence of limited reactant species, these systems allow for considerable control over the size and morphology of the particles synthesized in their cores. Reverse microemulsions have been used to produce small quantities of nanometer-scale particles that may be useful in catalysis.[4] Unfortunately the vast majority of water-in-oil microemulsions are only stable at low ionic strengths in the aqueous phase, making these systems unattractive for large scale powder production.

The microemulsion system we utilize is based on a isooctane continuous phase with the common surfactant, bis-(2-ethylhexyl)sulfosuccinate sodium salt (AOT), and water. Although nanocrystalline powders could be produced using this system, it proved to be undesirable for large scale powder production due to the common problem of low microemulsion stability at high ionic strengths of ferrous or ferric ion. Without modifications only milligrams of catalyst precursor were produced per liter of this microemulsion. This limitation was overcome when we found that addition of small amounts of a second common surfactant, sodium dodecylsulfate (SDS), stabilized the microemulsions at much higher ionic strengths. We found that by using the SDS co-surfactant, we were able to increase in the amount of precursor salt that could be dissolved in the aqueous phase while maintaining a stable microemulsion by over an order of magnitude (Table

I).[5] These new microemulsions, termed Modified Reverse Micelles (MRMs), have proven to be suitable systems in which to generate a variety of ultrafine metal oxides, metal sulfides, metals, and mixed materials (Table II) with reasonably high yields (≥ 10 g/liter).[5-7]

Essentially any particle precipitation reaction that can be accomplished in a bulk aqueous solution can be adapted for use with MRM systems. For example, magnetite can be synthesized at 80°C by addition of an MRM solution containing a mixture of ammonium hydroxide and ammonium nitrate (an oxidant) to an MRM solution containing ferrous sulfate.[6-8] Similarly, pyrrhotite can be produced by addition of an equivalent of a sulfide source (e.g. ammonium sulfide) to a MRM solution containing an equivalent of ferrous ion. Particle synthesis in the MRM system allows control over the crystallite growth, permitting production of a very fine and uniform powder product. Typically the powders produced by the MRM technique are highly reactive when cleaned of solvents and surfactants, reflecting their very high surface areas (>100 m^2/g). The small crystallite size and high surface areas are demonstrated by the instability of magnetite and pyrrhotite powders in air. Both magnetite and pyrrhotite produced by the MRM method rapidly oxidize upon exposure to air.

Rapid Thermal Decomposition of precursors in Solution. A second high capacity nanocrystalline powder synthesis method that was developed at PNL for this program is the Rapid Thermal Decomposition of precursors in Solution (RTDS).[6,9-11] RTDS is a flow-through method that utilizes brief exposures of metal-containing precursor solutions to high temperature, high pressure conditions followed by an abrupt thermal quench. The RTDS method is commonly used with water as the solvent, but can be adapted for use with a variety of nonaqueous media, including organic liquids, carbon dioxide, and ammonia.

The RTDS process evolved from another ultrafine powder formation process developed at PNL, the Rapid Expansion of Supercritical Solutions (RESS).[12] In RESS, the desired material is first dissolved in a supercritical fluid and the resulting solution is expanded through a nozzle. The solvent density drop that occurs during the expansion causes nucleation of the solute into finely divided powder. However, the iron oxides and sulfides of interest for this program proved insufficiently soluble in supercritical water to allow production of testable quantities of the catalysts by this method.

To produce iron oxide or oxyhydroxide powders for coal liquefaction catalysts by the RTDS method, dilute aqueous ferric salt solutions are pressurized and passed through a heated section of high pressure tubing (to fluid temperatures of 100°C to 400°C) with a residence time of less than 60 seconds (typically <10 s). Under these conditions hydrolysis of the metal species occurs very rapidly and uniformly, promoting production of ultrafine insoluble oxide or oxyhydroxide particles. The resulting suspension undergoes a rapid thermal quench as it is passed through a pressure reduction nozzle, thus stopping the particle growth. The nanometer-sized powders are then isolated using standard techniques such as centrifugation, spray drying, or freeze drying. The crystallite size of the materials produced by this method is governed mainly by the RTDS reaction temperature, but may also be directly affected by the precursor species (salt), additives, pH, *etc.* Conditions can be adjusted to allow formation of various phases of iron oxide by this method. Selected powders produced by the RTDS process are shown in Table III. Notice that seven of the ten common iron oxides have been synthesized by the RTDS technique demonstrating the utility of this technique for producing different phases of the same material. One of the best RTDS-generated catalyst precursor powders tested to date, 6-line ferrihydrite, was formed at 300°C using a feed solution 0.1 M in ferric nitrate and 1.0 M in urea.

Catalyst Testing

Preliminary evaluation of iron-based catalyst precursor powders were carried out using the model compound naphthyl bibenzylmethane (NBBM) and an established testing procedure.[13] In short, the procedure involved loading glass tubes with 25 mg of the model compound, the catalyst precursor (10 mg), elemental sulfur (10 mg), and pure 9,10-dihydrophenanthrene (100 mg). The tubes were sealed under vacuum, heated in a sand bath for 1 hour, opened, and the contents dissolved in methylene chloride. The products were analyzed by GC and GC/MS and quantified against an internal GC standard. Other model compounds have been used to investigate the mechanism by which the iron-based catalysts operate. These compounds include substituted diphenylmethanes, bibenzyl, and dibenzothiophene.

Effect of Catalyst Precursor Phase. A range of pure iron oxide and oxyhydroxide powers was prepared using published literature procedures in bulk aqueous solutions.[8] A systematic series of tests was undertaken using these bulk-synthesized powders to evaluate the effect of crystallite phase on catalytic activity in reactions with NBBM. The results of these studies suggest that crystalline phase is a critical factor in determining whether an iron oxide/oxyhydroxide powder will be catalytically active under liquefaction conditions (Table IV).[13] Catalyst precursor powders used for these tests were separated from solution, dried under a stream of nitrogen gas, and ground to fine powders with a mortar and pestle. The powders obtained were used without sieving. At a 400°C reaction temperature, ferric oxyhydroxysulfate (OHS) and 6-line ferrihydrite (6-line) were found to be particularly active precursor phases for consumption of the NBBM substrate. These results strongly indicate that certain crystallographic phases of iron oxide are more readily converted into the active catalyst phase (pyrrhotite) under our reaction conditions.

Effect of Preparation Method on Catalytic Activity The catalytic activity of the catalyst precursors generated by the MRM and the RTDS methods have been tested using the NBBM model compound.[6] In general, the activity dependence on the iron oxide phase observed with the literature prepared materials is also true for the nanometer-sized crystallites produced by RTDS and MRM. Table V shows testing results for selected RTDS and MRM powders with NBBM at 400°C using the standard testing conditions. The hematite and the 2-line ferrihydrite produced by the RTDS process both show little catalytic activity. The 6-line and the OHS both show the expected high activity. Many batches of 6-line and OHS produced by the RTDS methods gave similar results to those in Table V.

The catalytic activity of magnetite exhibits a strong dependence on crystallite size, which is related to the production method. The RTDS and the MRM produced magnetite shows enhanced C-C bond scission activity over bulk produced magnetite. Table VI shows these differences as a function of the crystallite size for RTDS produced magnetite. The RTDS magnetite is as good a catalyst as any tested including OHS and 6-line. No attempt has been made to correlate aggregate or agglomerate size to crystallite size for the magnetite samples. The increased catalytic activity may be more an effect of smaller aggregate size than crystallite size as is demonstrated for RTDS produced 6-line (see below). It should also be noted that the MRM 2-line ferrihydrite, while not being an exceptional catalyst, is much improved over the bulk and RTDS products.

Effects of Aggregate Size and Form. A major thrust of our research has been to synthesize catalyst precursor powders having nanometer-sized crystallites with the purpose of maximizing the number of available catalytic surface sites per gram of powder. In addition to crystallite size, however, we have seen that for some of the tested powders the size and/or form of the crystallite aggregates was an important parameter affecting the observed catalytic activity.[14]

The two best iron-based catalyst precursor powders generated by RTDS and bulk synthesis methods were sieved into +230, -230/+325, and -325 mesh fractions using ASTM standard procedures. Figure I shows the effect of mesh (aggregate) size on the activities of RTDS-generated 6-line and bulk-synthesized OHS on the catalytic consumption of the NBBM model compound. These results suggest that the catalytic activity of the 6-line material is highly dependent on the aggregate size, and that in an unsieved sample, the bulk of its observed activity comes from the smaller aggregates contained therein. When the -230/+325 mesh 6-line sample was ground in a mortar and resieved, the -325 mesh sample obtained also exhibited the high catalytic activity of the original -325 mesh sample. The effect of sieve size on catalytic activity of the 6-line powders was not unique to an isolated batch of powder or to 6-line powders produced only by the RTDS process. Several batches of 6-line ferrihydrite generated using standard bulk literature preparations and by different RTDS preps showed similar aggregate size/activity dependence. Activity of the OHS, however, was observed to be essentially independent of the sieve (aggregate) size.

The strong dependence between catalytic activity and aggregate size of the 6-line ferrihydrite and the lack of such a relationship for the OHS may reflect significant differences in the nature of the aggregates comprising the powders of these materials. When separated from suspension and dried, most of the iron oxide and oxhydroxide powders contain relatively dense aggregates of the individual nanocrystallites. These aggregates are relatively tightly bound and likely allow limited transport of substrate molecules to catalytic grain surface sites on their interiors. OHS, on the other hand, consists of small (<100 nm) spiculed spherical aggregates that are loosely agglomerated into larger features.[8] These larger agglomerates readily redisperse into the individual spherical features upon suspension in an organic fluid. Even in the form of the small spherical aggregates, the OHS crystallites are relatively open and accessible to the model compound substrates. The high dispersability and open structure of the aggregates in the OHS powders appears unique among the iron-based catalyst precursors tested.

Selectivity The selectivity of the all of the iron oxide precursors toward cleavage of bonds in the NBBM substrate was found to be similar. Catalytic consumption of NBBM yielded primarily naphthalene and methyl bibenzyl (from A bond cleavage), with lesser amounts of methyl naphthalene and bibenzyl (from B bond cleavage).[6,12] Essentially no other cleavage was observed to occur in NBBM with the iron-based catalysts. Unsymmetrically methyl substituted diphenylmethanes, 4-methyl diphenylmethane (MeDPM), 2,5-Dimethyl diphenylmethane (Me_2DPM), and 2,4,6-trimethyl diphenylmethane (Me_3DPM), used as model compounds were almost exclusively cleaved between the methylene carbon and the methylated aromatic ring.[15] Figure 2 shows the consumptions of the methylated DPM compounds with 4 different iron oxide precursors which had been sieved to -325 mesh. Again, OHS was superior to the other catalyst precursors evaluated. These results also suggest that a REDOX mechanism may be occurring as a rate determining step in the catalyzed bond cleavage as the amounts of model compound consumed increases with decreasing oxidation potential of the model compound.

Other model compounds tested with OHS and 6-line included diphenylmethane, bibenzyl, and dibenzothiophene. Little bond cleavage was observed in reactions with bibenzyl and diphenylmethane and no reactivity was observed in reactions with dibenzothiophene.

Correlation Between Coal and NBBM Results. We have performed evaluations of catalyst precursor activity using model compound reactions, primarily because of the relative ease of data work-up for the model compound reactions. A number of accurate model compound runs can be performed in the time a single coal liquefaction run is analyzed. The validity of using NBBM as a model for coal studies is illustrated in Figure 3. A good correlation is observed between the results of the NBBM consumption and the total THF solubles produced when the Argonne premium coal Blind Canyon Seam was reacted in the presence of the same catalyst precursors. Catalyst precursors exhibiting poor C-C bond scission with NBBM were typically also poor coal liquefaction catalysts. This confirms that NBBM is an appropriate test molecule for screening the iron-based catalysts for their coal liquefaction activity. In addition, model compound test results can be used to probe the mechanism of catalytic attack on the coal structure by evaluation of the model compound reaction products.

Catalyst Comparison and Scale-Up

The two most efficient catalysts at 400°C toward consumption of NBBM are OHS and 6-line ferrihydrite. The OHS precursor appears to be more active at 400°C and retains some of it's activity to 250°C while the 6-line rapidly loses activity with decreasing temperature. The OHS catalyst precursor consumes 90% of NBBM at 360°C while the 6-line falls from 89% consumption at 400°C to 67% at 360°C. The OHS is clearly a superior catalyst precursor at low operating temperatures. Unfortunately the literature preparation of OHS uses a 1 week dialysis time to yield less than 2 g/L. While the RTDS method is more efficient (only 1 one day dialysis time following RTDS), the yields are not much better (<50%). The 6-line literature preparation also involves a time consuming dialysis step but the RTDS process does not. Using the RTDS process 6-line yields of almost 100% are attainable without dialysis and the RTDS produced suspensions can be separated and dried directly after reaction. RTDS produced 6-line is also amendable to the co-processing of co-catalysts such as molybdenum, nickel, cobalt, *etc* or coatings such as sulfate with no loss in yields. For these reasons the 6-line ferrihydrite produced by the RTDS method has been chosen for scale-up and is currently being produced in tens-of-grams with scale-up to pound quantities under investigation.

Summary

New methods of nanocrystalline catalyst synthesis have been developed and are shown to be capable of producing highly active iron-based coal liquefaction catalyst precursors. Evaluation of a broad range of iron oxide and oxyhydroxide powders produced using standard bulk synthesis methods has indicated that at 400°C, the most active phases toward model compound consumption are 6-line ferrihydrite and ferric oxyhydroxysulfate. Highly active 6-line ferrihydrite powder can be produced in large quantities using the RTDS powder synthesis method. Activity of the 6-line ferrihydrite is found to be sensitive to its particle (aggregate) size, with activity of unsieved 6-line attributed primarily to the smaller aggregates present in the powder. Activity of the ferric oxyhydroxysulfate powder is found to be essentially independent of aggregate size and it retains catalytic activity to relatively low reaction temperatures. However, feasibility of using the OHS as a coal liquefaction catalyst is reduced by its time consuming synthesis.

Future Research Plans

In the near future large quantities of catalyst precursors will be synthesized by the RTDS process for testing in larger scale coal liquefaction reactors which will allow testing of the catalyst performance over long runs. Continued production and optimization of the catalyst precursors to produce the highest activity/gram material which are stable for transport and storage. Some emphasis will be placed on developing iron-based catalyst precursors capable of hydrodesulfurization and hydrodenitrofication in addition to cracking reactions. Optimization of the RTDS method for the production of OHS catalyst precursor will continue. In addition the mechanism of activity of the iron-based catalysts will continue to be investigated with the aim at understanding the factors involved in producing the highest activity catalyst possible.

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Table I

Total Metal Ion Concentration Acheivable in Standard Reverse Miceoemulsions and Modified Reverse Microemulsions (MRM)

Metal Ion	Concentration in Microemulsion
Fe^{3+}	< 0.01 M (Conventional Micelle)
Fe^{3+}	> 0.5 M (MRM)
Fe^{2+}	> 0.2 M "
Ni^{2+}	> 0.2 M "
Cu^{2+}	> 0.2 M "

Table II

Selcted Examples of Powders Produced Using Modified Reverse Micelles (MRM)

Isolated Powder		Crystallite Size
Ferrihydrite	($FeOOH$)	< 10 nm
Magnetite	(Fe_3O_4)	3-7 nm
Maghemite	(γ-Fe_2O_3)	12 nm
Trevorite	($NiFe_2O_4$)	< 10 nm
Pyrrhotite	(FeS)	< 10 nm
Pyrite	(FeS_2)	15 nm
Nickel Metal		1-2 nm
Cobalt Metal		31 nm
Hawleyite	(CdS)	< 10 nm
Cobalt/Molybdenum Oxide	($CoMoO_x$)	< 10 nm

Table III

Selected Examples of Powders Produced by RTDS Method

Isolated Powder		Grain Size	Surface Area
2-Line Ferrihydrite		< 10 nm	220 m^2/g
6-Line Ferrihydrite		< 10 nm	200 m^2/g
Hematite	(α-Fe_2O_3)	6-20 nm	180 m^2/g
Goethite	(α-$FeOOH$)	11 nm	
Magnetite	(Fe_3O_4)	< 12 nm	
Maghemite	(γ-Fe_2O_3)	15 nm	
Ferric Oxyhydroxysulfate		< 10 nm	
Trevorite	($NiFe_2O_3$)	< 10nm	
Tenorite	(CuO)	20 nm	
Bunsenite	(NiO)	12 nm	
Cubic Zirconia	(ZrO_2)	3 nm	428 m^2/g
Anatase	(TiO_2)	3 nm	

Table IV

Results of Reactions of Iron-Oxygen Compounds with Naphthyl Bibenzylmethane (NBBM) in the Presence of Sulfur and 9,10-Dihydrophenathrene at 400°C

Iron Phase	Chemical Formula	% Consumption NBBM	% Selectivity
Proto-Oxyhydroxides			
2-Line Ferrihydrite	Unknown	11 ± 4	73 ± 3
6-Line Ferrihydrite	Unknown	87 ± 3	97 ± 2
Ferric Oxyhydroxy-sulfate	$Fe_8O_8(OH)_8SO_4$	94 ± 3	95 ± 2
Oxyhydroxides			
Feroxyhyte	δ'-FeOOH	58 ± 10	94 ± 4
Akaganeite	β–FeOOH	80 ± 3	96 ± 2
Lepidocrocite	γ-FeOOH	70 ± 23	93 ± 3
Goethite	α-FeOOH	80 ± 10	90 ± 4
Oxides			
Hematite	α-Fe_2O_3	37 ± 5	81 ±4
Maghemite	γ-Fe_2O_3	11 ± 3	70 ± 10
Magnetite	Fe_3O_4	15 ± 2	67 ± 5
Wustite	FeO	15 ± 2	67 ± 3
Metal			
Iron Filings	Fe	13 ± 2	76 ± 2

Table V

Selected Examples of the Activity of RTDS and MRM Produced Catalyst Precursors with Naphthyl Bibenzylmethane. The Reactions Were Run at 400°C with Sulfur and 9,10-Dihydrophenthrene.

Catalyst	% NBBM Consumed	% Selectivity
MRM Products		
2-Line Ferrihydrite	51	91
Magnetite/Maghemite	77	89
Goethite/Lepidocrocite	44	93
RTDS Products		
2-Line Ferrihydrite	20	84
Hematite	23	83
Hematite/6-Line Ferrihydrite	81	96
6-Line Ferrihydrite	> 90	96
Magnetite	> 90	98
Ferric Oxyhydroxysulfate	> 90	96

Table VI
Effect of Crystallite Size on Catalytic Activity for RTDS Magnetite.
Consumption of NBBM at 400°C using Standard Test Conditions.

Magnetite Grain Size	% Consumption of NBBM
30 nm (Lit Prep)	16
12-19 nm	74
< 12 nm	>90

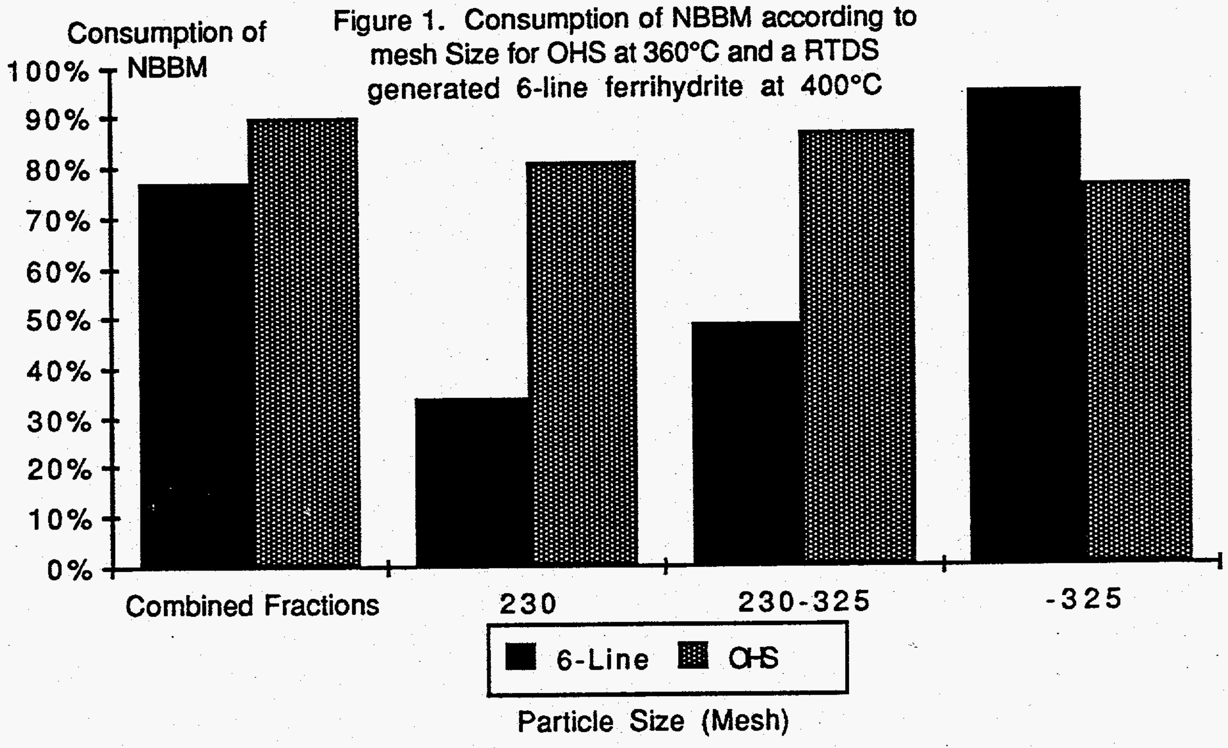
Figure 1. Consumption of NBBM according to mesh Size for OHS at 360°C and a RTDS generated 6-line ferrihydrite at 400°C

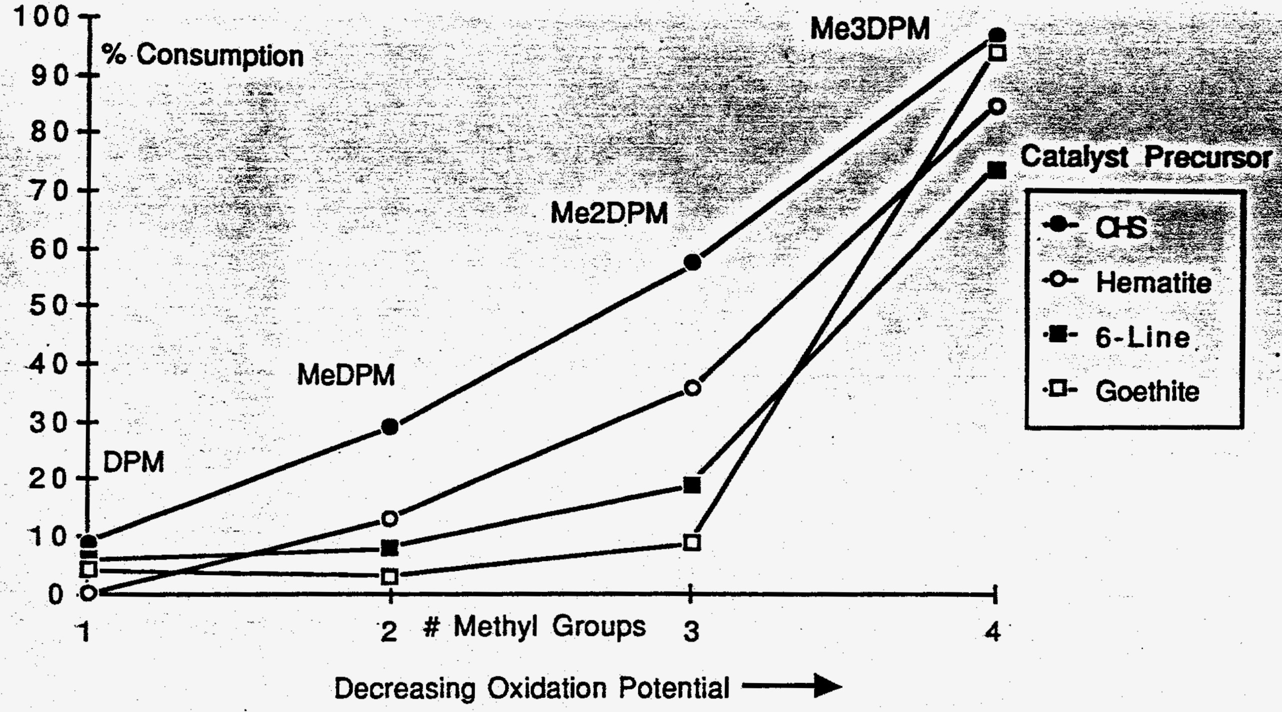

Figure 2. The dependence of model compound consumption with degree of methyl substitution on diphenylmethane with ferric oxyhydroxysulfate (OHS), hematite, goethite, and 6-line ferrihydrite (6-line) at 400°C. DPM is diphenyl methane, MeDPM is 4-methyldiphenylmethane, Me_2DPM is 2,5,-dimethyl diphenylmethane and Me_3DPM is 2,4,6,-trimethyl diphenylmethane.

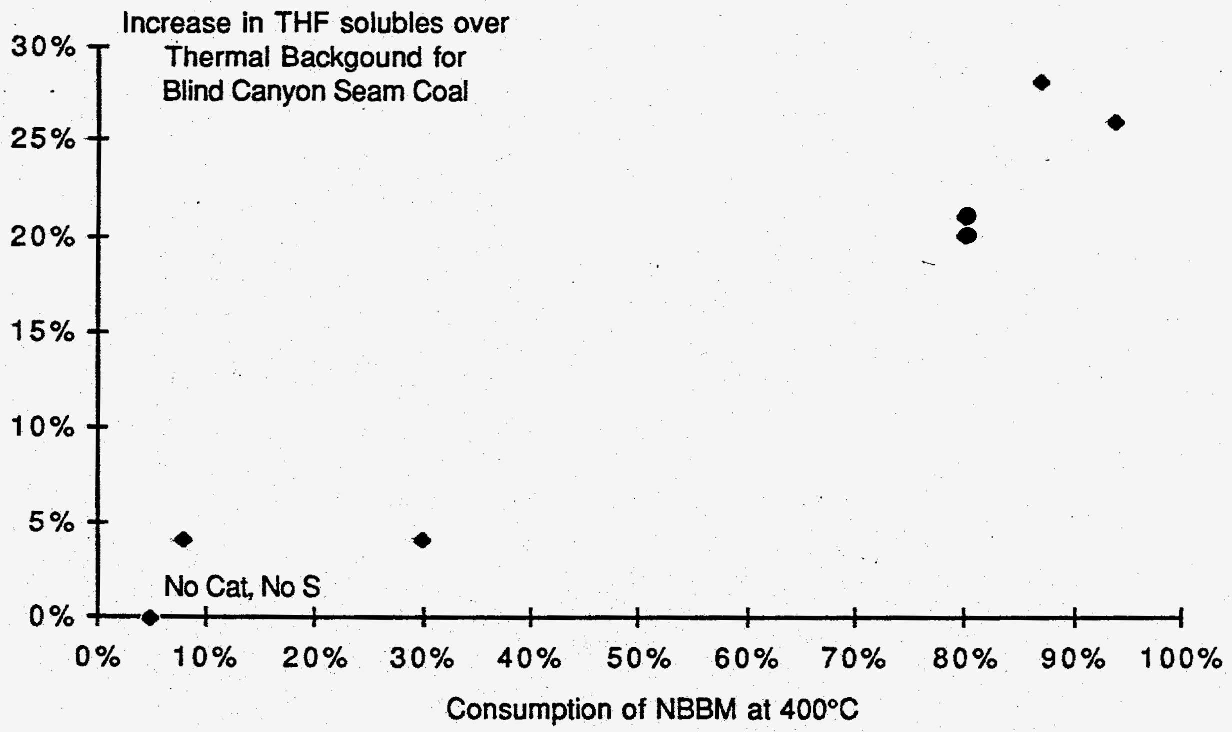

Figure 3. The correlation between the amount of THF solubles from reactions with Blind Canyon Seam coal and the amount of naphthyl bibenzylmethane consumed.