

## RESULTS OF CATALYST TESTING USING IRON-BASED CATALYSTS

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### ABSTRACT

New bulk and ultrafine iron-based coal liquefaction catalysts have been tested using coal substrates and a model compound. The results of these tests will be presented with emphasis on differences between bulk and ultrafine catalysts. The effects of catalyst size, surface area, and structure on both the model compound reactions and the coal liquefaction reactions will be compared. Special emphasis will be placed upon identifying the best catalyst precursor for optimizing THF soluble yields from coal experiments. In addition, results from different micro-reactors for coal liquefaction will be compared.

### INTRODUCTION

As coal liquefaction catalysts, iron-based products are generally inferior to the more expensive molybdenum, cobalt, or nickel-based materials. However, the lower costs of production and recovery (or in the case of some iron catalysts, non-recovery) give the iron-based materials a potential economic advantage over the more efficient precious and semi-precious metal catalysts for this application. Recent research has shown that a number of different iron-containing materials can be successfully utilized as coal liquefaction catalysts or as catalyst precursors.<sup>2-6</sup>

Pyrrhotite ( $Fe_{1-x}S$ ) or a similar iron-sulfide phase is commonly believed to be the active catalyst in coal liquefaction and model compound pyrolysis reactions,<sup>7</sup> although no specific phase has been yet been isolated as the actual catalyst species. The active iron-containing catalyst is usually generated *in situ* from an iron-oxide precursor and an elemental sulfur source under reducing conditions in the reactor vessel. Most research has concentrated on the use of common iron-oxide phases such as hematite or goethite (and their derivatives) as the iron-bearing precursor, or on non-specific iron materials produced by the reaction of various iron salts and compounds in the coal or liquefaction reactor. To our knowledge there has been no systematic effort to determine the optimum iron-containing precursor phase for producing active coal liquefaction catalysts, despite the fact that there are over ten iron-(hydroxy)oxide phases which can be easily synthesized in the laboratory.<sup>8</sup>

We have undertaken a systematic study to identify the most active iron-oxide catalyst precursor phases, the co-catalysts, and the coal pretreatments which will provide optimum yields in coal liquefaction processes. In this paper we present recent results of a study using a range of different authentic single phase iron-containing powders as catalyst precursors in coal model compound dissociation reactions. We also present the results of using ultrafine iron-containing powders synthesized by the Rapid Thermal Decomposition of Solutes (RTDS)<sup>9,10</sup> and Modified Reverse Micelle (MRM)<sup>11</sup> methods as precursors for catalysts in model compound reactions. Preliminary results of coal liquefaction runs using both fixed volume tubing bomb reactors and a flow through micro-liquefaction reactor are included.

### EXPERIMENTAL

The synthesis of iron-containing powders using MRM<sup>11</sup>, RTDS,<sup>9,10</sup> and standard laboratory procedures<sup>8</sup> has been described elsewhere. All iron-containing materials synthesized for use in this study were analyzed by X-ray diffraction (XRD) and other methods as appropriate. The model compound (naphthyl bibenzylmethane), its synthesis, and the test reactor conditions were also described previously.<sup>11,12</sup>

**Tubing Bomb Coal Liquefaction Runs** - Coal liquefaction studies were performed using the Wyodak and Blind Canyon Seam Argonne premium coals. The coal (1.2 g), iron-oxide catalyst precursor (0.01 g), and elemental sulfur (0.01 g) were loaded into 316 stainless steel tube reactors with 2 ml of tetralin and pressurized with 800 psi hydrogen. The total volume of the stainless steel vessel and the gas inlet was less than 6 ml. The vessels were placed in a fluidized sand bath at the selected temperature for a specified time. A thermocouple was placed in contact with the metal surface of the reactor, allowing indirect observation of the reaction temperature. The warmup times were typically 1 minute to 380°C, 5 minutes to 390°C and 10 minutes to 400°C. The temperature variation during an hour long run was  $\pm 3^\circ\text{C}$  once the reaction temperature was attained.

The reaction product was extracted with tetrahydrofuran (THF), and the dried insoluble residue was used to calculate the liquefaction yield. The THF extract was reduced in volume and precipitated with pentane to determine the amount of pentane insolubles. The pentane soluble fraction was calculated by difference. All yields are reported as moisture and ash free (maf).

**Micro-Liquefaction Reactor** - The micro-liquefaction reactor (Fig. 1) consisted of an in-line filter assembly attached to a HPLC pump and a capillary restrictor at the reactor exit for maintaining pressure. The stainless steel fritted cup was filled with the coal or coal/catalyst mixture, weighed, and sealed inside the micro-reactor body. Tetralin was pumped at 0.2 ml per minute through the assembly at a pressure sufficient to maintain the tetralin as a liquid at 400°C. The assembly was immersed in a fluidized sand bath at the desired temperature for the appropriate time. The dark colored tetralin fractions were collected continuously. After removal from the sand bath, tetrahydrofuran was pumped through the cooled micro-reactor until the color of the effluent was a light yellow. The coal residue was weighed after Soxhlet extraction with THF and drying. After cooling, the tetralin insolubles were filtered and weighed. Pentane was then added to the THF soluble fraction to precipitate the pre-asphaltenes, which were also filtered and weighed.

## RESULTS

Table I shows that most of the authentic laboratory-prepared oxyhydroxides, particularly lepidocrocite ( $\gamma\text{-FeOOH}$ ) and goethite ( $\alpha\text{-FeOOH}$ ), were better catalyst precursors than the oxides for carbon-carbon bond scission in naphthyl bibenzylmethane. Pure magnetite ( $\text{Fe}_3\text{O}_4$ ) and maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ) were found to be particularly poor catalyst precursors for this reaction. The proto-oxyhydroxide, 2-line ferrihydrite, was also determined to be a poor catalyst precursor for the model compound reaction. The organic products of the catalytic runs were almost exclusively methylbibenzyl and naphthalene (with some tetralin). The iron-containing products, while not rigorously characterized after the reaction runs, were typically observed as black solids with at least some ferromagnetic component.

Significant increases in the activity of the 2-line ferrihydrite, magnetite, and maghemite phases toward carbon-carbon bond scission in the model compound were noted when the materials were produced by the RTDS and the MRM methods (Table II). This increase in yields may have been due to smaller particle size or the presence of undetectable active phases in the initial catalyst precursors of the RTDS and MRM powders.

Selected coal liquefaction results utilizing tubing bombs (Table III) and using a MRM synthesized "iron-sulfide" catalyst showed that the reactivity of this catalyst appeared to change with the coal utilized. The results obtained using Wyodak coal showed an obvious improvement in both the THF soluble and the pentane soluble fractions obtained using this catalyst. There was, however, no statistical difference between the catalyzed and uncatalyzed runs when the Blind Canyon Seam coal was used with the MRM "iron-sulfide" catalyst.

The results of testing 2-line ferrihydrite catalyst precursors synthesized by the MRM method on both Wyodak and Blind Canyon Seam coals shown in Table IV. Again, a larger enhancement in the production of THF soluble products over thermal-only runs was noted when using the catalyst on the Wyodak coal. There was also an increase observed in the production of the pentane soluble fraction for both coals over the thermal-only runs when using the 2-line

ferrihydrate precursor.

Table V shows the Blind Canyon Seam coal liquefaction run results for a series of iron-oxides and oxyhydroxides produced by the RTDS method. A moderate increase in the total liquid products as well as a smaller increase in pentane solubles was observed with these catalyst precursors relative to the thermal-only run.

Figure 2 shows the liquefaction yields from Blind Canyon Seam coal when a 2-line ferrihydrate catalyst precursor produced by MRM was used in the flow-through micro-reactor. The total liquid yield in these runs was only slightly greater than in the non-catalyzed or sulfur-only thermal runs for this coal, but a definite difference was observed in the types of products formed when the flow-through reactor was used. The amounts of tetralin insolubles and pentane insolubles obtained in the catalyzed runs were significantly less than in the uncatalyzed runs.

## SUMMARY

The testing of authentic iron-(hydroxy)oxide phases with the naphthyl bibenzylmethane model compound demonstrated large differences in catalytic activity between the starting iron-containing species. Materials produced by MRM and RTDS promoted more reaction with the model compound than did the phases synthesized using literature procedures. Our testing with coals showed that ultrafine iron-oxyhydroxide powders produced by the RTDS and MRM methods were good catalyst precursors for coal liquefaction in the presence of sulfur.

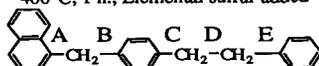
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TABLE I  
 MODEL COMPOUND REACTIONS  
 WITH AUTHENTIC IRON CONTAINING PHASES  
 400°C, 1 h., Elemental sulfur added



Naphthyl Bibenzylmethane

Catalyst	% Consumption	Selectivity <sup>a</sup>
<b>Controls</b>		
None	2-5%	40-60%
Sulfur Only	5-20%	50-70%
<b>Proto-Oxyhydroxide</b>		
2-Line Ferrihydrite	7%	71%
<b>Oxyhydroxides (FeOOH)</b>		
Feroxyhyte (δ)	45%	90%
Akaganeite (β)	14%	97%
Lepidocrocite (γ)	70%	93%
Goethite (α)	73%	92%
<b>Oxides</b>		
Hematite (α-Fe <sub>2</sub> O <sub>3</sub> )	37%	81%
Maghemite (γ-Fe <sub>2</sub> O <sub>3</sub> )	14%	86%
Magnetite (Fe <sub>3</sub> O <sub>4</sub> )	16%	54%

a) Selectivity is defined as [Products A + B Cleavage]/[Total Products]

Table II  
 MODEL COMPOUND RESULTS  
 WITH IRON-CONTAINING MATERIALS  
 PRODUCED BY RTDS AND MRM METHODS  
 400°C, 1 h., S added

Catalyst	% Consumption	Selectivity
<b>Controls</b>		
None	2-5%	40-60%
Sulfur Only	5-20%	50-70%
<b>RTDS</b>		
79-1 2-Line Ferrihydrite	49%	95%
79-4 Hematite	23%	83%
<b>MRM</b>		
39-39 2-Line Ferrihydrite	38%	90%
7-2 2-Line Ferrihydrite	51%	91%
7-2A Magnetite/Maghemite	77%	89%
9-2 "Iron-Sulfide"	68%	96%

**Table III**  
**Coal Liquefaction Results Using**  
**MRM-Derived "Iron-Sulfide" Catalyst Precursor and Sulfur.<sup>a</sup>**

Coal	Catalyst	% THF Soluble	% Pentane Soluble
Wyodak	None	71	39
Wyodak	9-2	85	46
BCS <sup>b</sup>	None	83	28
BCS <sup>b</sup>	9-2	85	28

a) Reaction conditions: 800 psi H<sub>2</sub>, 10 mg of sulfur, 400°C for 1 h.

b) BCS is Blind Canyon Seam.

**Table IV**  
**Reverse Micelle Derived 2-Line Ferrihydrite**  
**Catalyst Precursors Reactions with Coals<sup>a</sup>**

Coal	Catalyst	Liquefaction Temperature	% THF Soluble	% Pentane Soluble
Wyodak	None	400°C	71	39
Wyodak	7-2 + S	400°C	88	64
BCS <sup>b</sup>	None	350°C	58	23
BCS <sup>b</sup>	99-1 + S	350°C	63	32
BCS <sup>b</sup>	99-2 + S	350°C	62	30

a) Reaction conditions: 800 psi H<sub>2</sub>, 10 mg of sulfur, 1 h.

b) BCS is Blind Canyon Seam.

**Table V**  
**RTDS Derived Iron-Oxide Catalyst Precursors**  
**Reactions with Blind Canyon Seam Coal<sup>a</sup>**

Coal	Catalyst <sup>b</sup>	% THF Soluble	% Pentane Soluble
BCS <sup>c</sup>	None	83	29
BCS <sup>c</sup>	2-Line Ferrihydrite + S	87	30
BCS <sup>c</sup>	2-Line Ferrihydrite + S	91	30
BCS <sup>c</sup>	Hematite + S	91	35
BCS <sup>c</sup>	Hematite + S	93	36

a) Reaction conditions: 800 psi H<sub>2</sub>, 10 mg of sulfur, 400°C for 1 h.

b) Surface areas of catalyst precursors 180-215 m<sup>2</sup>/g as determined by BET.

c) BCS is Blind Canyon Seam.

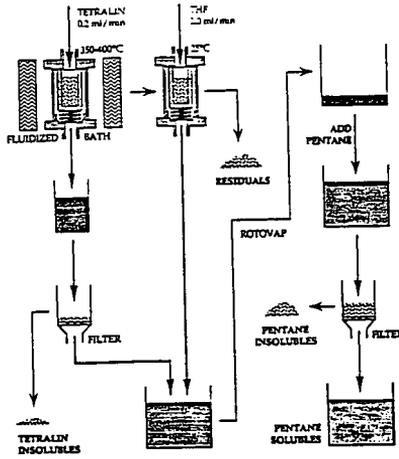


Figure 1. Schematic diagram of flow-through micro-liquefaction reactor and work-up method.

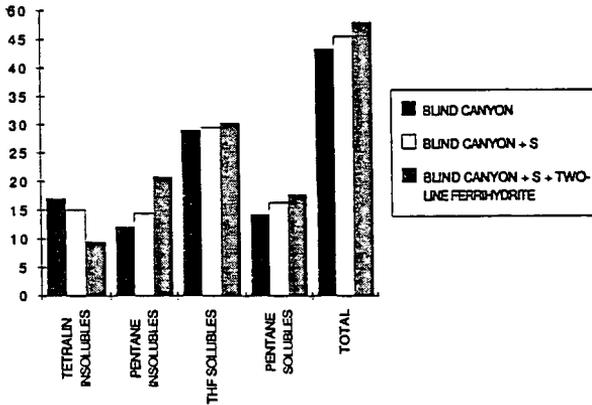


Figure 2. Liquefaction results of micro-liquefaction flow-through reactor with Blind Canyon Seam coal and a MRM synthesized 2-line ferrihydrite at 350°C for 1 hour with a 0.2 ml/min tetralin flow rate. Notice the large differences in the amount of tetralin and pentane insolubles between control and catalyzed runs.