

Task I

Iron-based Catalysts for Coal Liquefaction

Program Coordinators: Irving Wender and Gerald P. Huffman

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

TASK I

Project I.1

SULFATE-PROMOTED METAL OXIDES AS DIRECT COAL LIQUEFACTION CATALYSTS

Irving Wender, John W. Tierney, G.D. Holder
Chemical and Petroleum Engineering Department
University of Pittsburgh

Introduction

We have previously reported on the synthesis and characterization of a number of novel anion-modified sulfated and molybdated oxides and oxyhydroxides of iron (M_xO_y/SO_4 and M_xO_y/MoO_4)^{1,2,3}. These proved to be excellent catalysts for direct liquefaction of coal and coal-oil coprocessing reactions. Studies of these catalysts after reaction showed that the anionic modification of these iron oxide catalysts prevented their sintering at the high temperatures employed in coal liquefaction. When used in less than 0.5 -1.0 wt% Fe relative to coal and in the presence of a sulfur source, these catalyst precursors are effective for converting coal or coal-oil mixtures into light oils. In the past year, we have carried out several direct coal liquefaction experiments using Fe_2O_3 promoted by either sulfate, molybdate or tungstate anions and $Mo/Fe_2O_3/SO_4$ catalysts. We studied the effect of various reaction parameters on the total conversion and selectivity to oils. These included the effects of reaction temperature, reactor configuration, nature of the solvent, solvent-to-coal ratio and amount of sulfur added to the reaction mixture. We also presulfided some of the catalyst precursors and measured conversions in order to evaluate the possibility of catalyst reuse. Finally, we employed model compounds with anion modified metal oxides to improve our understanding of catalytic reaction pathways in direct coal liquefaction.

Experimental

All the direct coal liquefaction experiments were carried out using either a 27 cc horizontally shaken microreactor ('tubing bomb') or a 300 cc stirred autoclave

reactor. Temperatures of 375-425°C were used for coal liquefaction experiments with 800-1000 psig (cold) H₂ pressure. The normal reaction time was 60 minutes; reaction times between 5-120 minutes had been used for kinetic modelling. Coals used were obtained from the Argonne Premium Coal Sample Bank and from the Penn State Coal Sample Bank. Between 0.5-1.0 wt% of the anion-modified metal oxide catalysts (preheated to 450°C for 30 minutes before reaction) relative to coal were used in catalytic runs. Model compound reactions were all carried out in either the microreactor or in a 50 cc well-stirred microautoclave reactor.

Results and Discussion

Effects of Variation of Reaction Parameters on Total Conversion and Conversion to Oils

(i) *Effect of reaction temperature* : Three iron-based catalysts (Fe₂O₃, Fe₂O₃/SO₄, and Mo/Fe₂O₃/SO₄, all with added sulfur) were used for the direct liquefaction of Wyodak coal (0.17 % pyrite) at three different temperatures (375, 400 and 425°C) to determine the effect of reaction temperatures on the activities of these catalysts for coal conversion. As shown in Figure 1, the activities of the sulfated catalysts for the production of oils (n-pentane solubles) from coal increased proportionately in going from 375 to 425°C. Sulfated catalysts gave higher conversion and higher yields to oils than unsulfated iron oxide. Fifty ppm of Mo relative to coal, present in the Mo/Fe₂O₃/SO₄ catalyst, also had a significant effect on oil yields at 375°C.

(ii) *Effect of reactor configuration*: An important difference between the two reactor systems employed (the 27 cc microreactor and the 300 cc stirred autoclave) is the time required for heat-up and cooling. It takes about 35 minutes for the 300 cc autoclave to reach the reaction temperature (400°C and higher) and about 20 minutes to cool down to below 100°C after reaction. The microreactor can be heated up to reaction temperature in less than 5 minutes using a fluidized sand bath and cooled down immediately after reaction by quenching in cold water. Mass transfer effects may be different as the mixing phenomena are different in both systems. The results of the direct liquefaction of Argonne subbituminous Wyodak coal with tetralin (4:1 by weight to coal) as reaction solvent, and sulfated iron/tin oxide catalysts, using both the reactor systems, are shown in Figure 2. Both conversion and oil yields differ

by at most 6% and provide comparable results. The presence of excess amounts of donor solvent (tetralin), which provides a good dispersion medium for mixing and helps to maintain a H₂ rich atmosphere, may be responsible for the similar results observed from the two reactor configurations.

(iii) *Effect of solvent vehicle used and solvent-to-coal ratio:* Three solvents with different donor properties were used with sulfated iron oxide catalysts for direct liquefaction of Argonne Illinois No. 6 coal: Wilsonville recycle oil (V-1074), tetralin and 1-methylnaphthalene. The results are shown in Figure 3, from which it is evident that use of tetralin as the donor solvent gave the highest coal conversion and selectivity to oils. We believe that, in the presence of 1-methylnaphthalene, a non-donor solvent, the transformation of the initially added sulfated iron oxide precursor into its active catalytic form, pyrrhotite, is relatively slow. The effects of solvent-to-coal ratios on the conversion levels using sulfated iron oxide catalyst are shown in Figure 4. Conversion levels decrease with decreasing solvent-to-coal ratios. Since tetralin is a low-boiling solvent, much of it is in the vapor phase thus reducing the amount of liquid phase. Use of larger amounts of tetralin would hence provide a better dispersion and donor concentration in the liquid phase.

(iv) *Effect of amount of sulfur added to the reactor:* Sulfur is initially added to the reaction mixture; upon heating, the catalyst is transformed *in situ* to finely dispersed pyrrhotites (Fe_{1-x}S). The transformation may occur in the following way, where [Fe-O-S-H] is a transient



intermediate whose composition depends upon the reaction conditions. In the absence of sulfur, the coal conversions were slightly higher (5-6 wt%) than those obtained with a thermal blank run. When sulfur is added to the reactor to aid the *in situ* sulfidation of added catalysts, conversion levels increased by about 7-8 wt%. Sulfated iron oxide catalysts appear to perform more effectively with added sulfur.

(v) *Effect of presulfidation of the catalysts on coal conversion:* Presulfidation reactions were carried out at 400°C for 30 minutes in stirred autoclaves using tetralin as the reaction medium. A hydrogen donor is needed for rapid and complete catalyst transformation and the presence of carbonaceous material (from tetralin) on the

catalyst surface helps to maintain catalyst dispersion, mainly by inhibiting agglomeration⁴. The resulting iron catalyst was analyzed by X-ray diffraction, electron microscopy, and elemental analysis and was found to be primarily Fe_7S_8 ($\text{Fe}/\text{S} = 0.88$) with about 2 wt% of carbon deposited on its surface. This presulfided catalyst was then employed for the direct liquefaction of a low-pyrite Blind Canyon (DECS-17) coal, both with and without added sulfur. As shown in Figure 5, Fe_7S_8 gives conversions slightly better than those obtained with a thermal (only sulfur) blank run. Addition of elemental sulfur to the already presulfided catalyst improves its activity for coal liquefaction; it is about as active as the starting sulfated iron oxide with added sulfur. There seems to be no apparent advantage in presulfiding the catalyst. We believe that, not only pyrrhotites, but rather a combination of pyrrhotites and hydrogen sulfide is catalytically active for direct coal liquefaction.

Reactions with Model Compounds

To further understand the role of these catalysts in coal liquefaction, model compounds were used with these superacid anion-modified metal oxide catalysts at mild conditions to investigate the effect of superacidity of these catalysts during coal liquefaction. These reactions could provide an insight into acid-catalyzed reactions which may occur during the heat-up time involved in direct coal liquefaction. First, we used 5-benzyloxyindole as a model compound and reactions were conducted at temperatures of 250, 300 and 350°C with 1000 psig (cold) initial H_2 pressure. As expected, we observed cleavage of the C-O bond in 5-benzyloxyindole to form toluene in all the three reactions. But the GC-MS analysis of the pentane soluble products indicated no product other than toluene. This is probably because, after cleavage of the C-O bond in 5-benzyloxyindole, the remaining radical rapidly polymerizes to form a heavy product which is insoluble in pentane.

1-Phenyldecane was used as the model compound in most of our later reactions. Temperatures of 160-200°C and H_2 pressures (cold) of 300-500 psig were used in these experiments. A $\text{Mo}/\text{Fe}_2\text{O}_3/\text{SO}_4$ (1 wt%) catalyst preheated to 450°C for 30 minutes was added with 1-phenyldecane and the reaction was carried out in a horizontally shaken microreactor. After reaction time of 1 hour, the products were identified in a GC-MS and were later quantified using a gas chromatograph.

Though the overall conversion was low (about 10%), we found significant amounts of products formed due to alkylation of the benzene ring in 1-phenyldecane. The products ranged from singly substituted aromatics such as toluene to highly substituted multi-branched alkylbenzenes. The thermal reaction of 1-phenyldecane under these conditions produced no appreciable conversion. We attributed the hydrocracked and alkylated products to the acidity of the catalyst along with some hydrogenation ability. To further understand the role of catalyst acidity in these reactions, we synthesized a bimetallic Fe-Sn catalyst ($\text{SnO}_2/\text{Fe}_2\text{O}_3/\text{SO}_4$ containing equimolar amounts of SnO_2 and Fe_2O_3). This catalyst was earlier shown to have the highest acidity among all iron-based catalysts synthesized by our group⁵. This gave a slightly higher conversion of 1-phenyldecane than the Mo-Fe catalyst but the amount of alkylaromatics present in the products are yet to be analyzed. Preliminary experiments employing phenol and dodecane as the starting compounds with these catalysts gave products, a significant portion of which were alkylated phenols. Evidently, the superacidity of these catalysts is effective in alkylating aromatics whether or not a straight chain paraffin is attached to the aromatic ring. We plan to further investigate the role of catalyst acidity by using multiring compounds (with and without added sulfur) and then testing its effect on coal.

Major Findings

1. In the presence of sulfated iron-oxide catalysts and elemental sulfur, the coal conversion and the oil yields increased almost proportionately with increase in reaction temperature from 375°C to 425°C.
2. Tetralin proved to be a better coal liquefaction solvent than Wilsonville recycle oil (V-1074) or 1-methylnaphthalene in terms of both overall conversion and selectivity to oils. However, the amount of n-pentane soluble products (oils) obtained from the Wilsonville recycle oil and tetralin were almost the same.
3. As expected, the coal conversions and oil yields increased with increasing solvent-to-coal ratios. But the increase in conversions were less significant at high solvent-to-coal ratios.
4. Addition of increasing amounts of sulfur to the sulfated iron oxide catalysts during coal liquefaction runs increased the conversion and selectivity to oils.

Addition of more sulfur favors the *in situ* sulfidation of the sulfated iron oxide catalysts to form pyrrhotite, which is the active form of the catalyst.

5. Presulfiding the catalysts using tetralin as solvent in coal liquefaction did not show an apparent advantage, as the conversions and oil yields were almost the same as those obtained using sulfated iron oxide catalyst precursors.

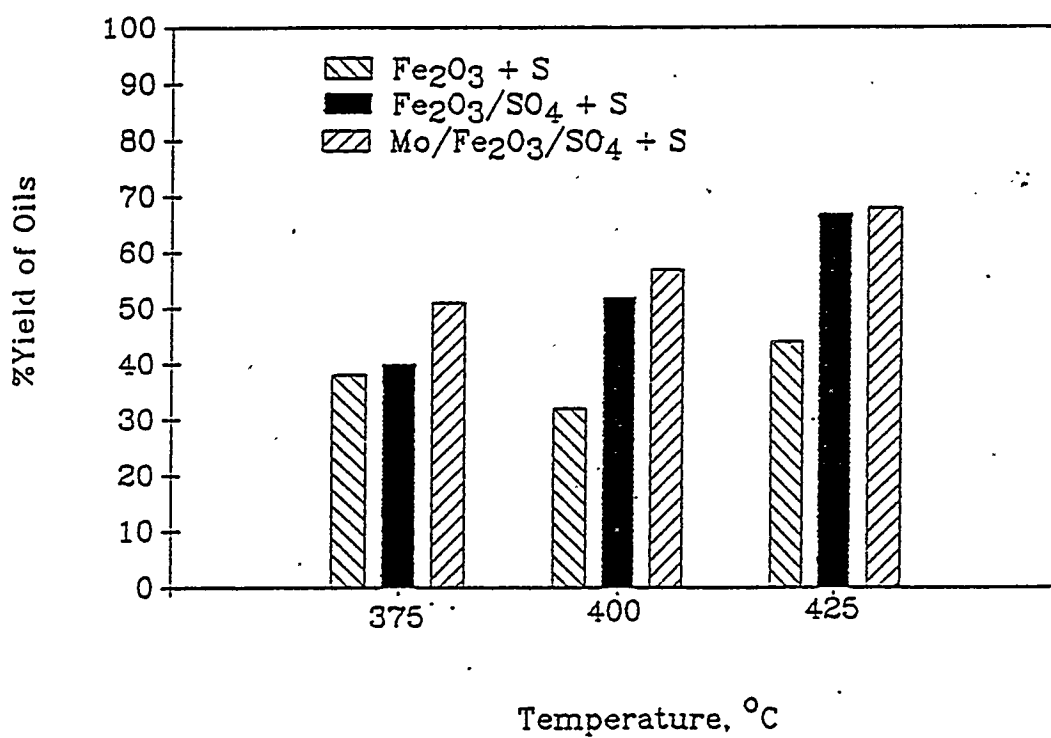
6. Model compound reactions at relatively mild conditions (160-200°C, 300-500 psig H₂) showed that the superacidity of these anion-modified iron and tin oxide catalysts plays an important role in hydrocracking and alkylation of 1-phenyldecane.

Future Work

We plan to investigate the anion-modified metal oxide catalysts in order to understand the acid-catalyzed reactions which occur at mild conditions using different model compounds. The next step is to introduce sulfur (both in organic as well as inorganic forms) into the model compound reaction systems and study the effect of sulfur on the quality of the products. The eventual objective of this investigation is to understand the effect of superacidity of these catalysts in direct coal liquefaction.

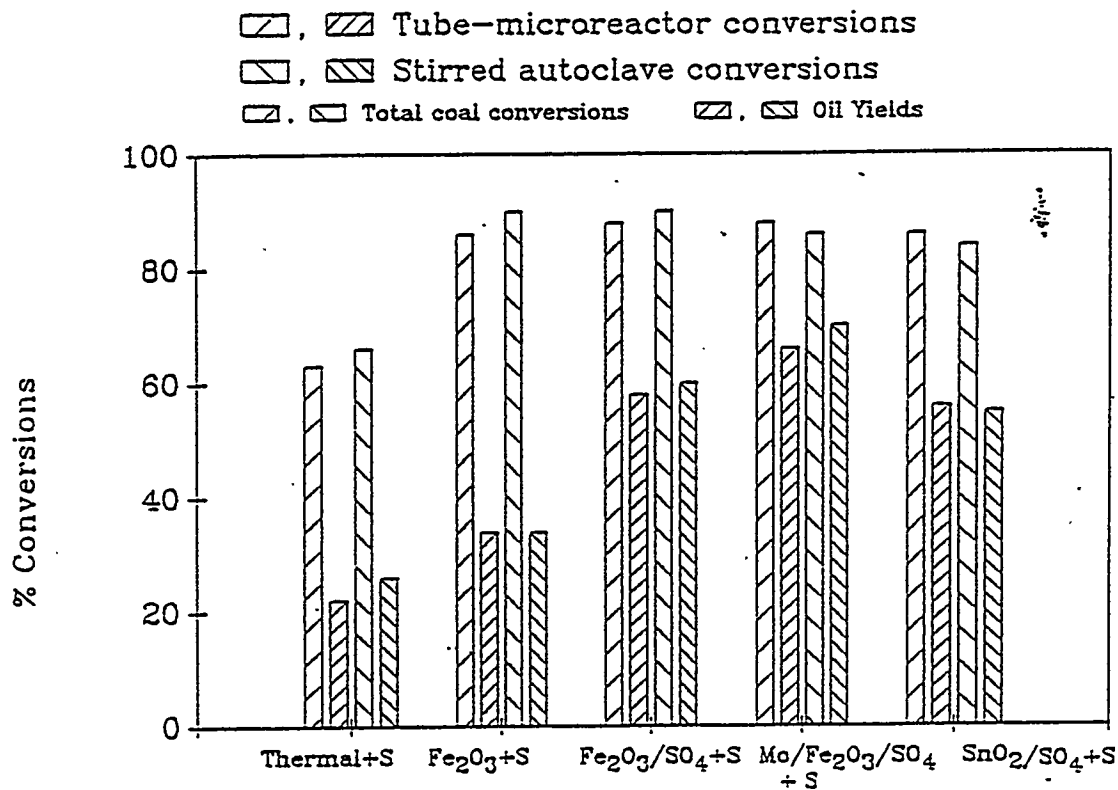
References

1. Pradhan, V.R., J.W. Tierney and I. Wender, Preprint., Am. Chem. Soc., Div. Fuel Chem., **37**, No.1, pp 254-261 (1992).
2. Pradhan V.R., G.P. Huffman, J.W. Tierney and I. Wender, *Energy and Fuels*, **5**, pp 497-507 (1991).
3. Pradhan V.R., D.E. Herrick, J.W. Tierney and I. Wender, *Energy and Fuels*, **5**, 712-720 (1991).
4. Andres, M., H. Charcosset, P. Chicke, L. Davignon, G. Marriadassou, J.P. Joly, S. Pregermain., *Fuel*, **62**, pp. 69-72 (1982).
5. Pradhan, V. R. "Catalysis by Novel Anion-modified Metal Oxides in Coal Liquefaction," Ph.D. Thesis, University of Pittsburgh (1993).



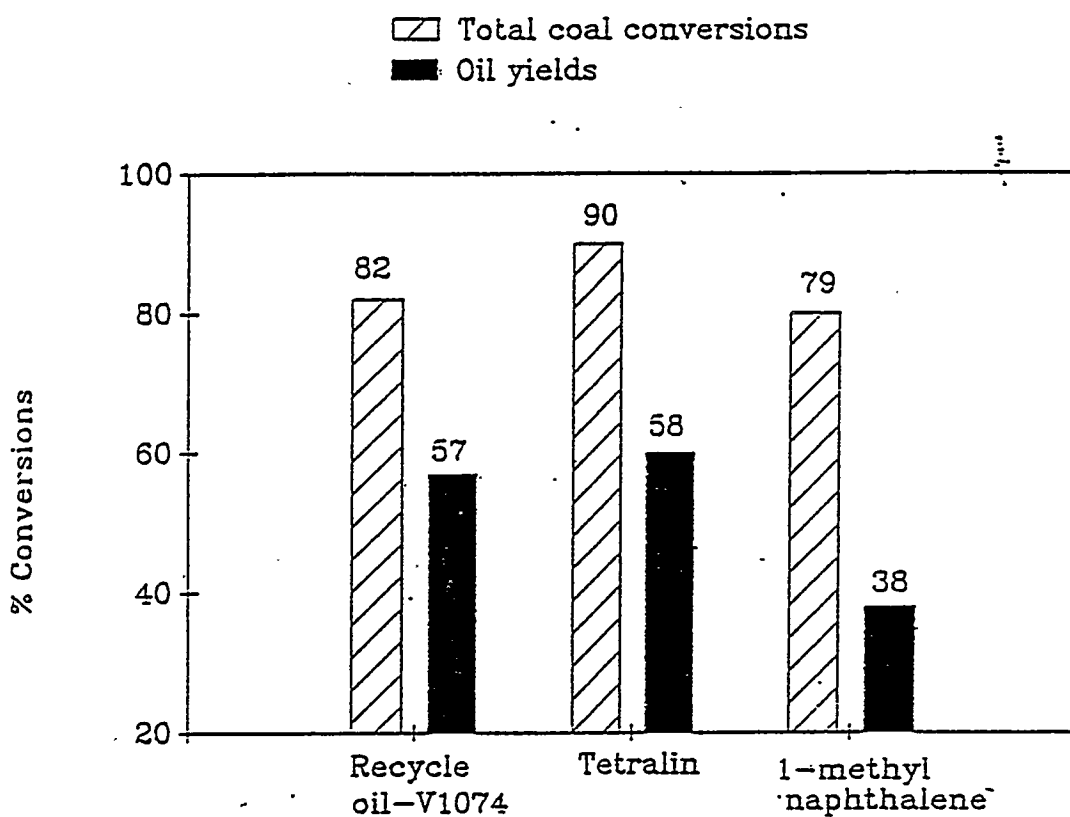
(Run Nos. KM-9, 4, 14, KM24, 19, 29, and KM39, 34, 44)

Figure 1 Effect of Reaction Temperature on the Activities of Sulfated Iron Oxides for Hydroliquefaction of Argonne Wyodak Coal at 1000 psig H₂, 1 hr Reaction Time.



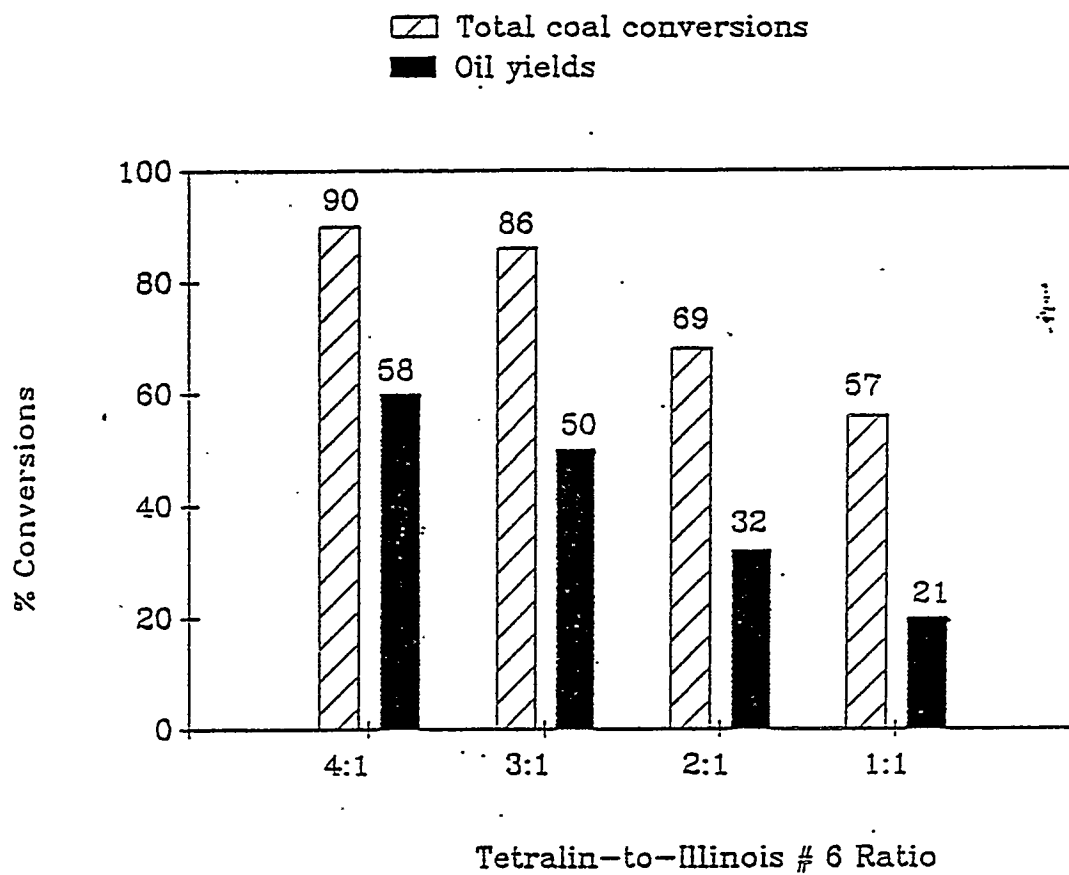
(Run Nos. MR02, KM9, KM24, KM39, and A062-A066)

Figure 2 The Effect of Reactor Configuration on the Conversion Levels using Argonne Wyodak coal and Tetralin, with Sulfated Iron Oxide Catalysts at 400°C and 1000 psig (cold) H₂, 1 hr Reaction.



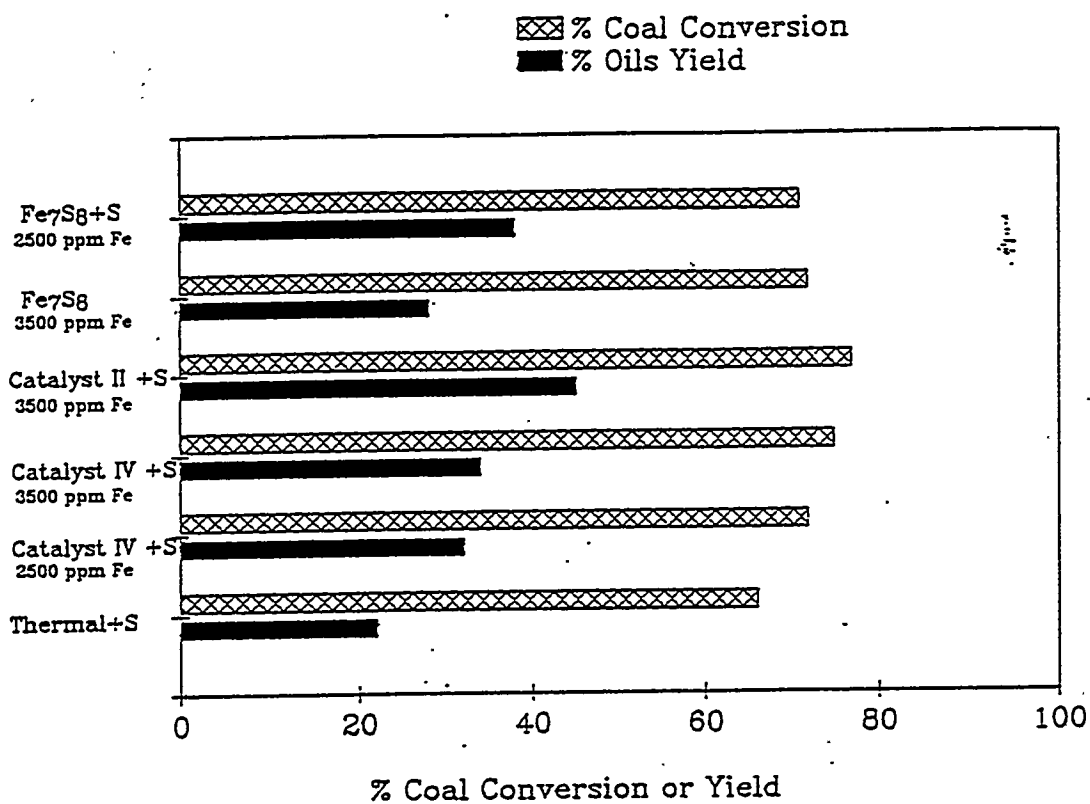
(Run Nos. A012, A059, and A060)

Figure 3 The Effect of Vehicle on Conversion Levels of Argonne Illinois No. 6 Coal using Sulfated Catalysts at 400°C, 1000 psig (cold) H₂, 1 hr Reaction.



(Run Nos. A012 and A056-A058)

Figure 4 The Effect of Solvent-to-Coal Ratios on Conversion Levels of Argonne Illinois No. 6 Coal using Sulfated Iron Oxide Catalysts at 400°C, 1000 psig (cold) H₂, 1 hr Reaction.



(Run Nos. A084-092)

Figure 5 Activities of the Fe₇S₈ Catalysts, Preformed by Sulfidation of Catalyst II, and of the Spent Sulfated Iron Oxide Catalyst for Hydroliquefaction of DECS-17 Coal at 400°C and 1000 psig H₂.

TASK I

Project I.2

LOW TEMPERATURE DEPOLYMERIZATION AND LIQUEFACTION OF PREMIUM COAL SAMPLES

Joseph S. Shabtai, W. Zmierzak and X. Xiao
University of Utah

The main lines of research during the May 1992 - April 1993 period were as follows:

1. Hydrogenolytic activity studies of soluble vs solid Fe-based catalysts using coal-simulating compounds as feeds.
2. Comparative hydrogenolytic activity studies of soluble vs solid Fe-based catalysts as related to coal liquefaction efficiency in the HT-BCD depolymerization procedure.
3. Preliminary studies on the depolymerization and co-processing of waste polymers.

Following is a short description of results obtained in the above studies.

I.1.1. Hydrogenolytic Activity Studies of Soluble and Solid Fe-Containing Acid Catalysts using Coal-Simulating Model Compounds.

A comparative activity study of soluble vs solid Fe-containing acid catalysts for hydrogenolysis of coal-simulating model compounds, i.e., 2-isopropylnaphthalene (IPN), 1,2-dinaphthylethane (DNE) and diphenylmethane (DPM), was performed. The soluble catalysts were supported on inert SiO₂ and included aqua complexes of various salts, i.e., sulfate, acetate and chloride. The solid catalysts consisted of finely dispersed superacids, i.e., Fe₂O₃/SO₄²⁻ and ZrO₂/SO₄²⁻. The activity of the soluble catalysts is ascribed to the aqua complex ion [Fe(H₂O)₆]³⁺, which is pre-formed or formed *in situ* in the presence of water, and

could act as a protonic acid by ligand dissociation.

Table I.1.1 summarizes the values of the pseudo-first-order kinetic rate constants (k_1) for hydrodealkylation of 2-isopropyl-naphthalene, IPN, to yield naphthalene and propane (see Figure I.1.1), as a function of catalyst type. Table I.1.1 also provides the values of the rate constants (k_2) for the competing ring hydrogenation of IPN to yield 2-isopropyl-1,2,3,4-tetrahydronaphthalene. Kinetic runs were performed at two different temperatures, i.e., 350 and 400°C. The k_1 values obtained were taken as a measure of the hydrogenolytic activity of the catalysts.

As seen, at 350°C the solid superacid catalysts 4 and 5 showed markedly higher activity for hydrogenolysis of IPN than the supported soluble catalysts 1 and 2. The difference in activity becomes larger with increase in reaction temperature from 350 to 400°C. The supported anhydrous $\text{Fe}(\text{CH}_3\text{COO})_3$ catalyst showed the lowest activity among the soluble Fe salt catalysts. Addition of a small amount of water to this catalyst (see footnote d, Table I.1.1) prior to reaction, resulted in some hydrogenolysis activity, which, however was lower than that of catalysts 1 and 2 that contain the pre-formed aqua complex $\text{Fe}(\text{H}_2\text{O})_6^{3+}$. The latter has been previously indicated²³ as the precursor of active, protonic acid-generating species, e.g., $\text{H}^+[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^-$. The relatively low activity of catalyst 3, even in the presence of water, indicated that it is preferable to use pre-formed aqua complexes of Fe salts. The thermal stability of such catalysts between 250-400°C is presently being investigated in this laboratory. The very low values of the ring hydrogenation rate constants (k_2) with the supported soluble catalysts 1-3 indicated that the latter possess essentially no ring hydrogenation activity, viz., they act as selective, monofunctional hydrogenolysis catalysts. In contrast, the $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ catalyst 4 showed moderate ring hydrogenation activity, especially at

400°C ($k_2=0.30$). This would indicate that under reaction conditions (H_2 pressure; elevated temperature) the sulfated iron oxide may be converted to a bifunctional catalyst system containing not only a strongly acidic functional group, but also a moderately active ring hydrogenation co-catalytic component. This could explain the overall good efficiency of this catalyst under coal liquefaction conditions.

Parallel hydrogenolytic activity studies with diphenylmethane (DPM) as feed showed similar trends as those in Table I.1.1. However, the rate constants for hydrogenolytic cleavage of DPM (to yield benzene and toluene) were lower, due to the slower protonation rate of the monocyclic aromatic rings in DPM, as compared with that of the bicyclic arene system in IPN.

Another model reaction studied was hydrogenolysis of 1,2-dinaphthylethane, DNE (Figure. I.1.2, reaction a). This reaction is accompanied by competing thermolysis (Figure I.1.2, reaction b). The composition of products from this feed showed the simultaneous occurrence of the above two main competing reactions, i.e., normal protonic acid-catalyzed α -cleavage leading to naphthalene and ethylnaphthalene and thermal cleavage at the β -bibenzylic position, to yield methylnaphthalene. The bibenzylic position has a very low bond dissociation energy (<70 kcal/mol).

Table I.1.2 provides the kinetic data obtained for the hydrogenolysis of 1,2-dinaphthylethane. Hydrogenolytic α -cleavage rate constants, k_α , were calculated on the basis of the yield of naphthalene and ethylnaphthalene (plus dimethylnaphthalene isomers). Table I.1.2 includes also rate constants, k_β , for the thermal β -cleavage reaction which were calculated from the yield of methylnaphthalene. Kinetic runs were performed at 325 and 350°C. The k_α rate constants obtained at these two temperatures indicated basically similar

trends as those observed for hydrodealkylation of 2-isopropylnaphthalene at 350 and 400°C. Both at 325 and 350°C the solid superacid catalysts showed higher hydrogenolytic activities as compared with those of the supported soluble catalysts 1 and 2. At 325°C the activity of $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ was only moderately higher than that of the catalysts 1 and 2. However, the difference in activity of the two groups of catalysts increased markedly when the reaction temperature was elevated to 350°C. Differences in the k_β values for the thermal (noncatalytic) β -cleavage reaction were relatively small for all reaction runs at a given temperature. As expected, the k_β values were basically dependent only on the reaction temperature and the presence of a catalyst during the reaction had essentially no effect on the β -cleavage rate constants.

I.1.2. Comparative Hydrogenolytic Activity Studies of Soluble vs Solid Fe-Based Acid Catalysts as Related to Coal Liquefaction Efficiency.

The hydrogenolytic activity of the two types of catalysts, as reflected in their efficiency for coal depolymerization by the HT-BCD procedure, was also examined.

Table I.1.3 summarizes the total conversions of the Blind Canyon coal sample (DECS-17) into depolymerized, THF-soluble products obtained by HT-BCD treatment, using different acid catalysts in the HT reactor (a flow reactor system was used in this part of the study). As seen, using either the soluble aqua complexes of Fe salts (unsupported; impregnated in the coal) or solid superacids (in the form of fine dispersions with a mean diameter of approximately 130 Å; physical mixture with the coal) resulted in a very high level of depolymerization (92.4-94.5 wt.%, calculated on the (THF) pre-extracted DECS-17 coal sample; MAF basis). However, the impregnated aqua complexes can be applied as acid catalysts at a mild HT temperature (275-300°C) whereas the use of finely dispersed solid superacids in the HT treatment step requires temperatures of $\geq 340^\circ\text{C}$.

Table I.1.4 summarizes data on the distribution of the total HT-BCD products using various acid catalysts in the HT step of the coal depolymerization procedure. As seen, the yields of cyclohexane-solubles (oil fractions) using the impregnated aqua complexes as catalysts in the HT step are in the range of 63-69 wt %, whereas with the dispersed solid $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ catalyst the yield is somewhat lower (58.7 wt %).

The above described studies (Section I.1.1 and I.1.2) allow for the following conclusions:

Kinetic studies of acid-catalyzed hydrogenolysis of 2-isopropyl-naphthalene, 1,2-dinaphthylethane and diphenylmethane show that (in the temperature range of 350-400°C) finely dispersed solid superacids, e.g., $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ and $\text{ZrO}_2/\text{SO}_4^{2-}$, possess markedly higher hydrogenolytic activity as compared with that of soluble aqua complexes of Fe salts, e.g., Fe sulfate, chloride and acetate (supported on SiO_2).

In agreement with the above, it is found that finely dispersed solid superacids, in very low concentrations (0.1-0.5 wt.%), can be conveniently applied as hydrogenolysis catalysts in the HT step of the HT-BCD (mild hydrotreatment-base catalyzed hydrolysis) coal depolymerization process. The effective application of such superacid catalysts, e.g., $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$, in this process, however, requires HT temperatures $\geq 340^\circ\text{C}$, which are considerably higher than those previously found as optimal for impregnated soluble Fe salts as hydrogenolysis catalysts (275-300°C).

I.1.4. Preliminary Studies on the Depolymerization and Co-Processing of Waste Polymers.

Preliminary experiments on co-processing of a HVB coal (DECS-17) with a rubber sample of the SBR type (and in parallel runs with a sample of polyethylene) were performed using (a) $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ as catalyst at 300°C and a H_2 pressure of 1500 psig, i.e., conditions similar to those usually employed in the HT step of the HT-BCD coal depolymerization

procedure; or (b) $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ as catalyst at 340°C and a H_2 pressure of 2600 psig. These runs were followed by the usual BCD treatment at 290°C (10% KOH in MeOH as catalyst-solvent system). In both two-step (HT-BCD) treatments the yield of THF-soluble products was nearly proportional to the amount of the coal (70%) in the coal-SBR mixture, indicating practically no reaction of the SBR feed component under the above relatively mild conditions. Similar results were obtained with polyethylene as polymer component of the feed.

To identify suitable catalyst and processing conditions for high-yield conversion of waste polymers into liquid products, experimental work is being initiated on the catalytic breakdown reactions of pure polymers of the following types: (a) polystyrene samples with well defined molecular weights in the range of 800 to 280,000; and (b) isotactic polypropylene.

The effect of various acid, base, and organometallic catalysts in a wide range of processing conditions will be determined.

Table I.1.1.
**Kinetic Rate Constants for Hydrogenolysis (Hydrodealkylation) and
 Ring Hydrogenation of 2-Isopropyl-naphthalene (IPN) as a Function of
 Catalyst Type^{a-d}**

Catalyst		$k_1 \times 10^2$ (ml/g ^o min), hydrodealkylation		$66k_2 \times 10^2$ (ml/g ^o min), ring hydrogenation	
		350 C	400 C	350 C	400 C
FeCl ₃ .6H ₂ O/SiO ₂	(1)	3.9	31.5	0.2	0.7
Fe ₂ (SO ₄) ₃ .5H ₂ O/SiO ₂	(2)	2.4	10.6	0.4	1.3
Fe(CH ₃ COO) ₃ /SiO ₂ ^d	(3)	0.4	6.9	0.2	0.5
Fe ₂ O ₃ /SO ₄ ²⁻	(4)	6.2	99.2	4.2	30.0
ZrO ₂ /SO ₄ ²⁻	(5)	372.5	565.9	4.1	5.7

^a In each kinetic run was used 20 g (26.7 ml) of a 2.0% by weight solution of IPN in n-dodecane.

^b The amount of SiO₂-supported soluble catalysts 1, 2 and 3 used in each run was 4 g. The rate constants for these catalyst were calculated on a SiO₂-free basis. The amount of superacids 4 and 5 used in each run was 5000 ppm (0.5%).

^c Reaction conditions: H₂ pressure, 1500 psig; temperature, 350 or 400°C; microclave reactor volume, 50 ml; sampling time intervals, 5-10 min; total reaction time, 75 min.

^d A calculated amount of water, needed for *in situ* formation of the Fe(H₂O)₆³⁺ ion was added to this supported anhydrous salt, prior to reaction.

Table I.1.2
Kinetic Rate Constants for Hydrogenolysis of 1,2-dinaphthylethane as
a Function of Catalyst Type ^{a-c}

Catalyst		$k_{\alpha} \times 10^2$ (ml/g ² min), hydrogenolysis (α -cleavage)		$k_{\beta} 10^4$ (min ⁻¹), thermal cleavage (β -cleavage)	
		400 C	350 C	400 C	350 C
FeCl ₃ ·6H ₂ O/SiO ₂	(1)	1.7	5.9	0.8	9.4
Fe ₂ (SO ₄) ₃ ·5H ₂ O/SiO ₂	(2)	2.3	5.2	0.9	8.7
<hr/>					
Fe ₂ O ₃ /SO ₄ ²⁻	(3)	3.7	30.6	1.2	11.1
ZrO ₂ /SO ₄ ²⁻	(4)	37.4	89.9	1.1	9.8

^a In each kinetic run was used 25 g (28.8 ml) of a 2% by weight solution of DNE in toluene.

^b The amount of SiO₂-supported soluble catalysts 1 and 2 used in each run was 4 g. The rate constants for these catalysts were calculated on a SiO₂-free basis. The amount of superacids 4 and 5 used in each run was 5000 ppm (0.5%).

^c Reaction conditions: H₂ pressure, 1500 psig; temperatures, 325 and 350°C; microclave reactor volume, 50 ml; sampling time intervals, 5-10 min; total reaction time, 75 min.

Table I.1.3.
HT-BCD Treatment of Blind Canyon Coal (DECS-17) Using Different
Acid Catalysts in the HT Reactor^a

HT catalyst	Catalyst/feed ratio	HT temp., °C	Total HT-BCD conversion ^b
Fe ₂ (H ₂ O) ₅ (SO ₄) ₃	1:9	300	92.7
Fe(H ₂ O) ₆ Cl ₃	1:9	300	94.1
Fe ₂ O ₃ /SO ₄ ²⁻	1:200	340	92.4
ZrO ₂ /SO ₄ ²⁻	1:200	340	94.5

^a In each run was used 10.0 g of coal-catalyst mixture. HT reaction conditions: H₂ pressure, 1500 psig; H₂ flow rate, 50 sccm; total reaction time, 2 h. BCD reaction conditions: catalyst-solvent system, 10% KOH solution in MeOH; temperature, 290°C; total reaction time, 1 h.

^b Total yield of THF solubles (MAF basis), calculated on the pre-extracted Blind Canyon coal feed. The total yield of THF pre-extracted was wt%.

Table I.1.4.
Effect of Different HT Step Catalysts on Product Distribution
of HT-BCD Treated Blind Canyon Coal (DECS-17)^a

HT catalyst	HT temp., C	<u>HT-BCD product distribution</u>	
		Oil fraction ^b , wt%	Oil fraction ^b , wt%
Fe ₂ (H ₂ O) ₅ (SO ₄) ₃	300	63.2	36.8
Fe(H ₂ O) ₆ Cl ₃	300	68.5	31.5
Fe ₂ O ₃ /SO ₄ ²⁻	340	58.7	41.3

^a In each run was used 10.0 g of coal-catalyst mixture, HT reaction conditions: H₂ pressure, 1500 psig; H₂ flow rate, 50 sccm; total reaction time, 2 h. BCD reaction conditions: catalyst-solvent system, 10% KOH solution in MeOH; temperature, 290°C; total reaction time, 1 h.

^b Cyclohexane-solubles

^c Cyclohexane-insolubles, THF-solubles.

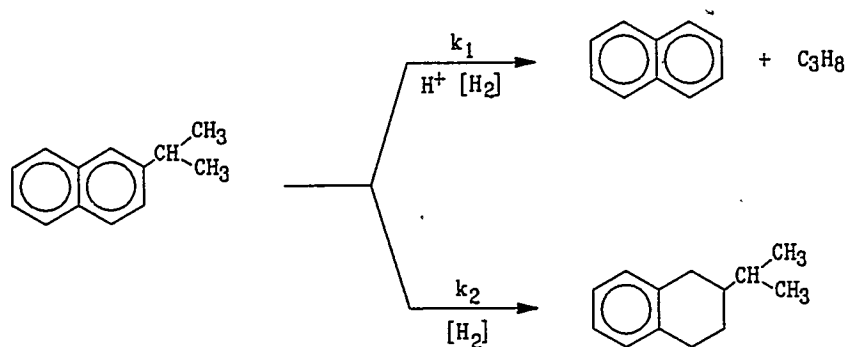


Figure I.1.1. Kinetic scheme of hydrodealkylation (k_1) and ring hydrogenation (k_2) of 2-isopropylnaphthalene (IPN).

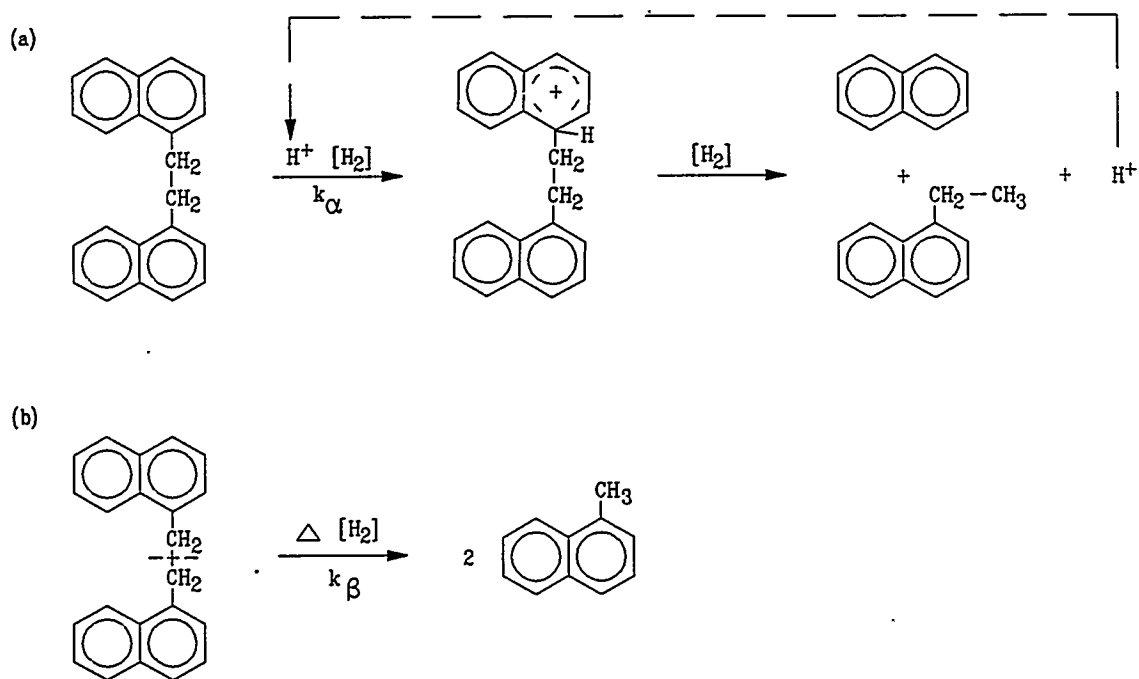


Figure I.1.2. Kinetic scheme of competing (a) hydrogenolysis and (b) thermolysis reactions of 1,2-dinaphthylethane (DNE).