

Task IV

Novel Catalysts for Coal Liquefaction

Program Coordinators: Christine Curtis and Dady Dadyburjor

TASK IV

Project IV.1

CATALYTIC DEHYDROGENATION OF MODEL COMPOUNDS IN RELATION TO COAL LIQUEFACTION

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Introduction

Hydrogen donor and transfer reactions are of major importance in the direct liquefaction of coal (DCL). Studies of the catalytic dehydrogenation of coal and recycle solvents can provide valuable information on the ease of hydrogen transfer from hydroaromatic entities and from solvents to coal; the objective is to achieve insights into the chemistry of DCL. Catalytic dehydrogenation can be coupled with ^1H -NMR analysis to obtain information on possible structural properties of coal and recycle solvents during conversion to oils. The quality of recycle solvents, in terms of hydrogen donor ability, are related to their behavior in DCL.

The rate of evolution of hydrogen and the amount of H_2 evolved from coal by catalytic dehydrogenation could be an indication of the activity of the catalyst in DCL, suggesting that catalytic dehydrogenation may be developed as a rapid way to assess the activities of DCL catalysts. We hope to relate the rate of hydrogen removal from hydroaromatics to their reactivities in DCL as well as to the activities of DCL catalysts. Research on catalytic dehydrogenation may help us select good recycle solvents and catalysts for DCL.

The objectives of the present work are (i) to determine the fate of hydroaromatic hydrogen during catalytic dehydrogenation and donor abilities of recycle solvents, (ii) to search for possible mechanistic pathways in catalytic dehydrogenation, (iii) to explore the possibility that catalytic dehydrogenation can be used as an analytic method for determination of the activity of DCL catalysts and (iv)

to obtain information on the fate of hydrogen atoms attached to various polynuclear hydroaromatics during the liquefaction of coal.

Results and Conclusions

On the Nature of Hydrogen Transfer in Catalytic Dehydrogenation and Coal Liquefaction

Researchers have shown that coal conversion is influenced by the amount, and especially the quality, of donor solvents^[1]. It has also been suggested that catalytic dehydrogenation of hydroaromatics of coal may be a useful method to gain insight into catalysis of coal liquefaction^[2]. In the latter case, no direct evidence has been obtained to correlate catalytic dehydrogenation and coal liquefaction. The following discussion is based on comparing the rate of hydrogen removal from 9,10-dihydroanthracene (9,10-DHA) and from 9,10-dihydrophenanthrene (9,10-DHP), two commonly used hydrogen donor solvents; this work may contribute to our understanding of hydrogen transfer during coal liquefaction.

We have previously found that 9,10-DHA evolves hydroaromatic hydrogen to the gas phase more readily than 9,10-DHP, with either Pd/C or with MoS₂, a good DCL catalyst. Can this finding be related to different hydrogen donor abilities of the two isomeric hydrocarbons? Care must be taken to distinguish between hydrogen evolution to the gas phase and actual hydrogen transfer to an acceptor. The transfer of hydrogen from donor solvent to coal is an effective step in coal conversion to form lighter molecular entities; however, hydrogen evolution as molecular hydrogen may be a wasteful use of hydrogen in coal conversion. A crucial step in DCL is to stabilize radicals by providing hydrogen from donor solvents. It was thought informative to investigate the catalytic dehydrogenation activity of a mixture of 9,10-DHA and 9,10-DHP in the presence of a hydrogen acceptor such as stilbene.

When 9,10-DHA and 9,10-DHP were dehydrogenated individually in the absence of hydrogen acceptor, 9,10-DHA tended to lose molecular hydrogen more rapidly than 9,10-DHP. A series of catalytic dehydrogenation experiments were run with equal weight fractions of 9,10-DHA and of 9,10-DHP in the presence of only a half equivalent of stilbene. The curves shown in Figure 1 are revealing. The

decrease in weight fraction of 9,10-DHP and stilbene follows a similar trend; the two curves overlap almost during the whole run. The amount of molecular hydrogen increases proportionally with the increase in the anthracene weight fraction, implying that 9,10-DHA may be responsible for most of the hydrogen evolved to the gas phase. It is clear that 9,10-DHP tends to transfer more hydrogen to an acceptor whereas 9,10-DHA is more likely to lose molecular hydrogen to the gas phase.

The performance of the two hydroaromatic structures under coal liquefaction conditions was examined in experiments in which the concentration of the hydrogen donor compounds was carefully controlled. A 2:1 solvent to coal ratio was employed in the liquefaction of Illinois No. 6 coal to provide enough hydrogen to avoid recondensation of thermally produced radicals. A comparison of the values reported in Table 1 indicates that the loss of hydrogen to the gas phase from 9,10-DHA is significant; higher conversion and oil yields are obtained with 9,10-DHP as donor solvent. The better liquefaction performance of 9,10-DHP suggests that the reaction involves more hydrogenation and hydrogenolysis as compared with the use of 9,10-DHA. The higher liquefaction reactivity of 9,10-DHP can be explained by its ability to function as a good hydrogen transfer agent that can transfer hydrogen to coal at the right conditions of temperature and pressure.

Characterization of Hydrogen Donor Ability of Coal, Recycle Solvents and Heavy Oils

On the basis of the above findings, the hydroaromatic hydrogen content and hydrogen donor ability of DCL resids furnished by Consol Inc. were compared by catalytic dehydrogenation using quinaldine as the vehicle in the presence of a hydrogen acceptor. The samples listed in Table 2 consists of THF-soluble 850°F+ distillation resids. The samples were produced at the Wilsonville pilot plant and the HRI, Inc. bench unit and were chosen to represent variations in processing conditions. As shown in Table 3, the total amounts of hydrogen removed from samples 5 and 7 exceed that obtained from the others, but the amount of hydrogen transferred to a hydrogen acceptor is less, indicating that these two samples may not be effective in hydrogen utilization for DCL. It is noteworthy that the amount of hydrogen transferred from samples 3 and 4 to the hydrogen acceptor (stilbene) is

significantly higher although the total hydrogen removed is less. This is probably because samples 3 and 4 have higher contents of hydroaromatics. The $^1\text{H-NMR}$ analysis shows considerable increase in aromatic content in keeping with the amount of hydrogen transferred. It is reasonable to predict that the hydrogen donating efficiencies of samples 3 and 4 are better than the other resids. As far as DCL behavior is concerned, we predict that samples 3, 4 and 8 will be the best recycle solvents.

Catalytic dehydrogenation of Illinois No. 6 coal and characterization of the dehydrogenation residues by $^1\text{H-NMR}$ were conducted to identify structural changes in relation to DCL. Both phenanthridine (b.p. 350°C) and quinaldine (b.p. 248°C) were used as solvents and the reactions were interrupted at different time intervals to obtain partially or completely dehydrogenated residues for NMR analysis. Interestingly, as shown in Figure 2, the total hydrogen transferred to the hydrogen acceptor with quinaldine as solvent is comparable to the amount of H_2 gas evolved when phenanthridine is used as the solvent. All the residues were then characterized by $^1\text{H-NMR}$ to ascertain structural changes after dehydrogenation. Table 4 shows that the aromaticity of the coal residue increases proportionally to the amount of H_2 evolved. It appears that selective removal of hydroaromatic hydrogen occurred under the conditions employed.

When a heavy oil (North slope $725^\circ\text{F}+$) was dehydrogenated, the amount of hydrogen transferred to the acceptor at 248°C was always less than the amount of H_2 gas evolved at 350°C . Heavy oils contain saturated naphthenic polycyclic structures which are probably difficult to dehydrogenate. Other structures in heavy oils may be responsible for the excess of hydrogen evolved at higher temperatures. Three model compounds--cholestane, cholesterol and cholesterol stearate--whose molecular arrangement is believed to resemble some of the structures present in the heavy oil, were dehydrogenated with quinaldine and with phenanthridine as vehicles, respectively. No hydrogen was evolved from the fully saturated polycyclic compound, cholestane, even at 350°C . However, the other two substrates readily gave off hydrogen at 350°C , but none was evolved at 248°C . It was confirmed by GC-MS and $^1\text{H-NMR}$ that compounds containing an aliphatic hydroxyl or a single double bond in

a polynaphthenic structure could play a role in the release of hydrogen at high temperature. It is possible that compounds with structures resembling cholesterol, with isolated double bonds in one or more rings, are present in heavy oil. This could account for the difference in hydrogen yield when heavy oil was catalytically dehydrogenated by the different vehicles.

These results show promise that catalytic dehydrogenation, coupled with ^1H -NMR analysis, may be a valuable analytical technique to assess the amount and the nature of hydroaromatic hydrogen in coal, recycle solvents and petroleum residues.

Assessment of Activity of Coal Liquefaction Catalysts by Means of Dehydrogenation

Procedures employed for determining the activity of coal liquefaction catalysts (under DCL conditions) are complex and time consuming. A relation between the activity of Mo or Fe catalysts for DCL and that for catalytic dehydrogenation of model compounds has not been previously addressed. We found we could predict the activity of some DCL catalysts by measuring the rate of hydrogen removal from hydroaromatic compounds in catalytic dehydrogenation with phenanthridine as solvent.

Essentially no hydrogen was transferred to stilbene when DCL catalysts (Mo and Fe sulfide) were used in dehydrogenation of 9,10-DHA; evidently stilbene is not adsorbed on the Mo and Fe catalysts. The activities of Mo and Fe sulfides were compared by measuring the amounts of hydrogen evolved as H_2 gas. The percentages of theoretical hydrogen evolution from 9,10-DHA observed using several DCL catalysts are plotted against time in Figure 3. Initial experiments with pyrite (FeS_2) as catalyst showed a slow hydrogen evolution rate; reduction of FeS_2 with hydrogen improved the activity of these catalysts. The amount of hydrogen evolved greatly increased on pretreatment of FeS_2 with hydrogen. The hydrogen evolution rate is significantly enhanced with pyrrhotite, Fe_7S_8 , as catalyst.

Molybdenum and iron sulfides are good coal liquefaction catalysts, with molybdenum more effective than iron. In catalytic dehydrogenation, MoS_2 exhibits excellent activity in the dehydrogenation of model compounds. A quantitative comparison was conducted with a mixture of 20% MoS_2 and 80% Fe_7S_8 as

dehydrogenation catalysts. All the hydroaromatic hydrogen was evolved as hydrogen gas, suggesting that a small amount of molybdenum is active enough to catalyze dehydrogenation. To substantiate this, only 0.1 gram of MoS_2 was used in the dehydrogenation of 9,10-DHA. Comparison of the hydrogen yield from using MoS_2 , Fe_7S_8 , and a mixture of MoS_2 and Fe_7S_8 catalysts shows that 0.1 g of molybdenum sulfide is about as active a dehydrogenation catalyst as 0.5g of pyrrhotite. If the activities of iron and molybdenum for dehydrogenation reactions on a metal loading basis are compared, it is found that molybdenum is about six times more active than iron as a catalyst for dehydrogenation. This activity ratio of Mo to Fe correlates well with that obtained from activity comparisons of molybdenum and iron sulfide in direct coal liquefaction.

Of course, the ratio of the activity of the two catalysts would undoubtedly vary somewhat with the use of other model hydroaromatic compounds as substrates and different solvents in catalytic dehydrogenation. Indeed, when 9,10-DHP, an isomer of 9,10-DHA, was used as the substrate in catalytic dehydrogenation, it was found that, as with 9,10-DHA, molybdenum sulfide was more active than iron sulfide (Figure 4). It is also interesting to find that the rate of hydrogen evolution with 0.2g of MoS_2 and 0.6g of Fe_7S_8 are nearly identical. In this experiment, Mo is about four times as active as iron, corresponding well with the result from dehydrogenation of 9,10-DHA. Catalysts such as MoS_2 and Fe_7S_8 , which are active for direct coal liquefaction, have similar relative activities for catalytic dehydrogenation of the model compounds studied. It appears that there is a relationship between the activities of Mo and Fe in catalytic dehydrogenation to their activities in DCL.

Future Work

Different ranks of coal, recycle solvents and heavy oils will be dehydrogenated in the presence of a hydrogen acceptor, stilbene, and the products will be analyzed by NMR to help in understanding the chemistry involved in coal liquefaction. The hydroaromatic content and donor abilities of the asphaltenes obtained from DCL and from the pretreatment of heavy oils will be examined by catalytic dehydrogenation coupled with $^1\text{H-NMR}$ analysis with the objective of establishing a quantitative

measure of donatable hydrogen in various substrates.

References

- [1]. Harrison, G. and K. Bate, Proceedings of International Coal Conference, Newcastle England, 739-742 (1991).
- [2]. Mochida, I., A. Takayame, R. Sakata and K. Sakanishi, **Energy & Fuels**, 4, 81 (1990).

Table 1. Effect of Donor Solvents on Liquefaction of Illinois No. 6 Coal

Donor solvent	Total Conversion of Coal*	Oil yield	Donor solvent converted to aromatics (wt%)
9,10-dihydrophenanthrene	77.6	23.7	66.0
9,10-dihydroanthracene	70.2	21.2	84.6

* Reaction conditions: 400°C, 1000 psig of He, Solvent/Coal=2:1, and 60 minutes in a microreactor.

Table 2. Description of DCL Resids Obtained from Consol Inc.

Ref. No.	Seam	Mine	Source	Designation	Comments
3	Pittsburgh	Ireland	W; Run 259	V-131B	Resid Composite
4	Pittsburgh	Ireland	W; Run 259	V-131B	THF-Soluble Resid Composite
5	Wyodak and Anderson	Black Thunder	W; Run 262B	V-131B	Resid
6	Wyodak and Anderson	Black Thunder	W; Run 262B	V-131B	THF-Soluble Resid
7	Wyodak and Anderson	Black Thunder	H;Run CC-2-14	PFL	THF-Soluble Resid
8	Wyodak and Anderson	Black Thunder	H;Run CC-15-9ABC	PFL	THF-Soluble Resid

Note: W=Wilsonville; H=HRI; all Wilsonville samples are from vessel V-131B (recycle stream); all HRI samples are pressure filter liquids (PFL).

Table 3. Comparison of Hydrogen Donor Abilities of Recycle Solvents with Quinaldine as Vehicle in the Presence of Stilbene.

Sample*	H content (wt%)	Hydroaromatic H by ¹ H NMR (wt%)	Total H removed (cc/gram)	H-transferred to stilbene (cc/gram)	H ₂ evolved as H ₂ (cc/gram)	% hydrogen transferred to stilbene
3	6.5	24.3	138.2	68.9	69.3	49.9
4	6.74	24.3	139.3	70.0	69.3	50.2
5	7.6	21.6	190.6	49.3	141.3	25.9
6	8.19	22.4	159.0	61.7	97.3	38.8
7	8.16	19.7	200.7	48.7	152.0	24.3
8	7.46	18.4	174.0	71.3	102.7	41.0

a. Samples are the distillation resids from DCL furnished by Consol Inc. The volume of hydrogen was measured at 25°C, 740 mm Hg.

Table 4. Characterization of Residues from Catalytic Dehydrogenation of Illinois No. 6 Coal

Run Time(min)	Aromatic/Hydroaromatic Hydrogen by ¹ H-NMR	Amount of Hydrogen evolved (ml/g)*
60	42.9	112.5
120	68.6	161.5
180	88.9	212.0
210	96.1	227.5

* Reaction conditions: Pd/CaCO₃ as catalyst, phenanthridine as solvent, H₂ was measured at 25°C, 744 mmHg.

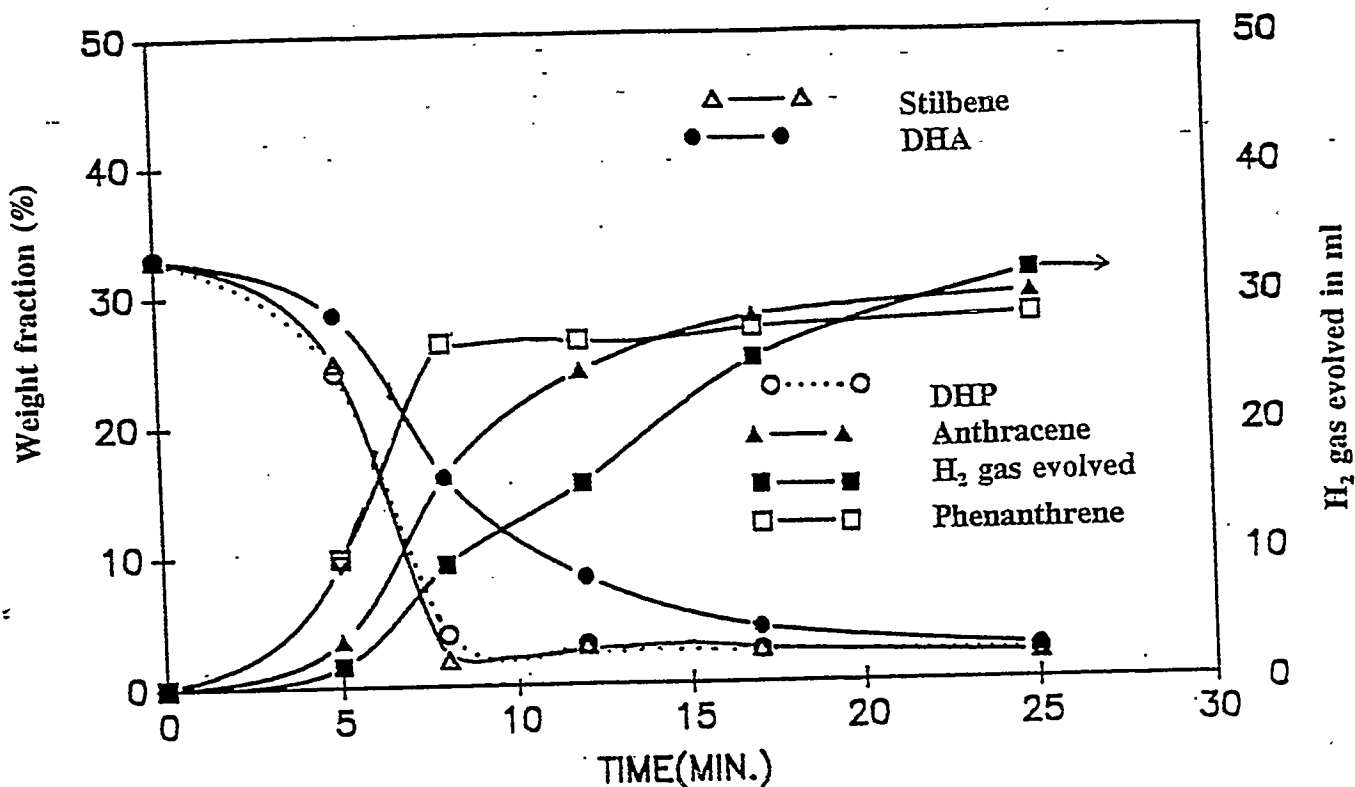


Figure 1. Dehydrogenation of a mixture of 9,10-DHA and 9,10-DHP in presence of half an equivalent of hydrogen acceptor with Pd/C as catalyst, quinaldine as vehicle.

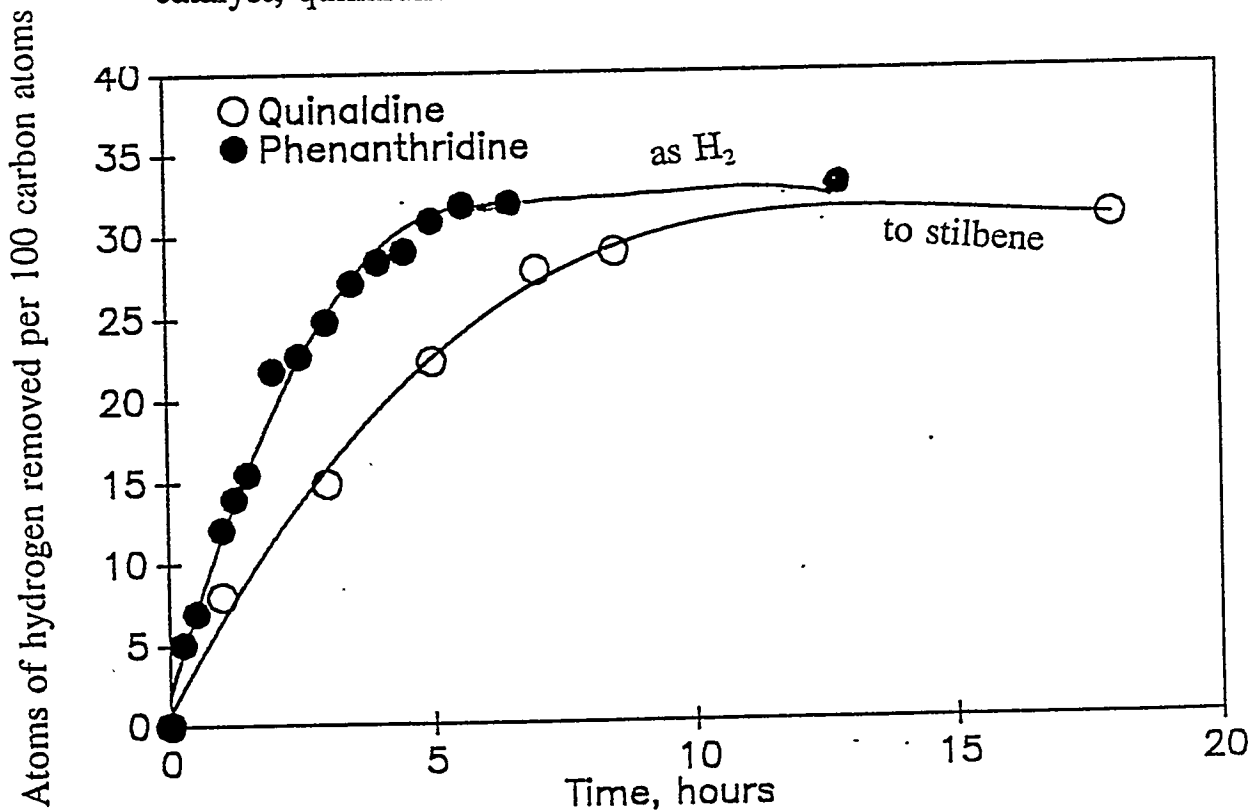


Figure 2. Determination of the hydroaromatic content in Illinois no.6 coal using different vehicles.

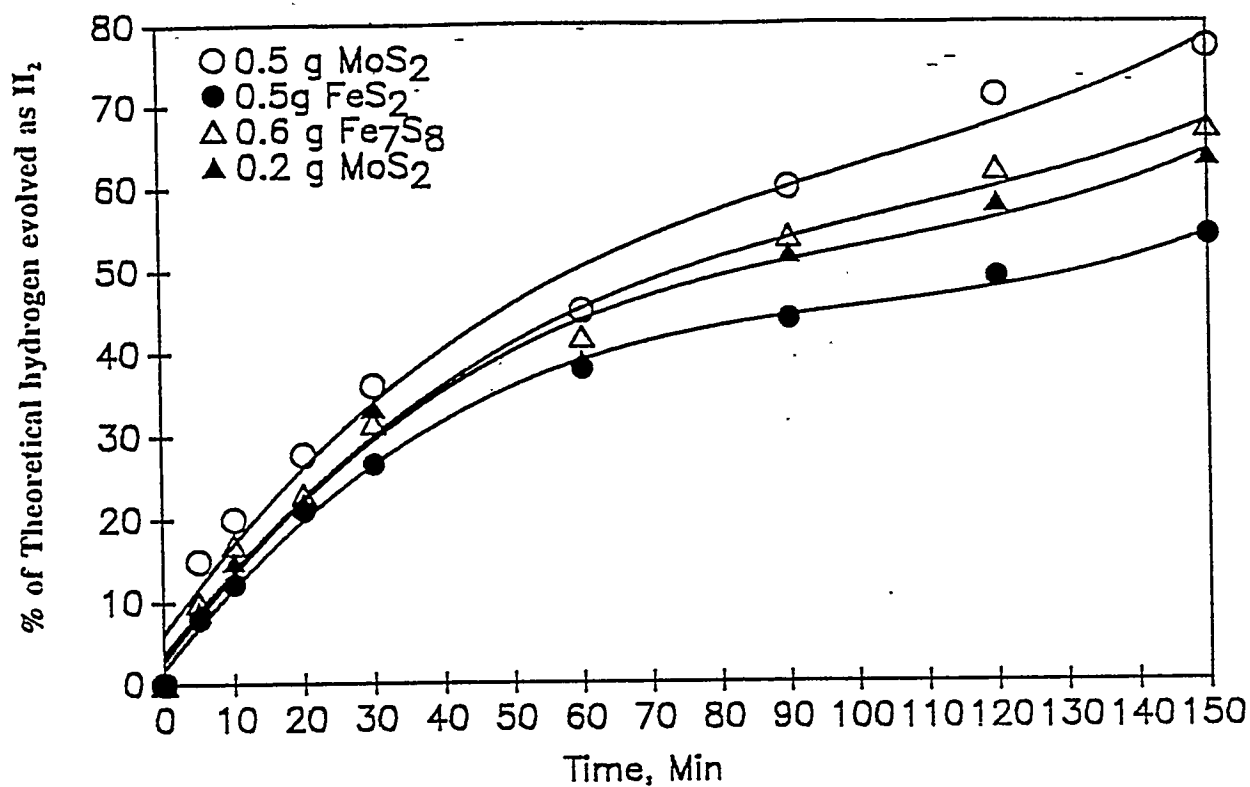


Figure 3. Evolution of molecular hydrogen from 9,10-DHA in presence of DCL catalysts, phenanthridine as vehicle.

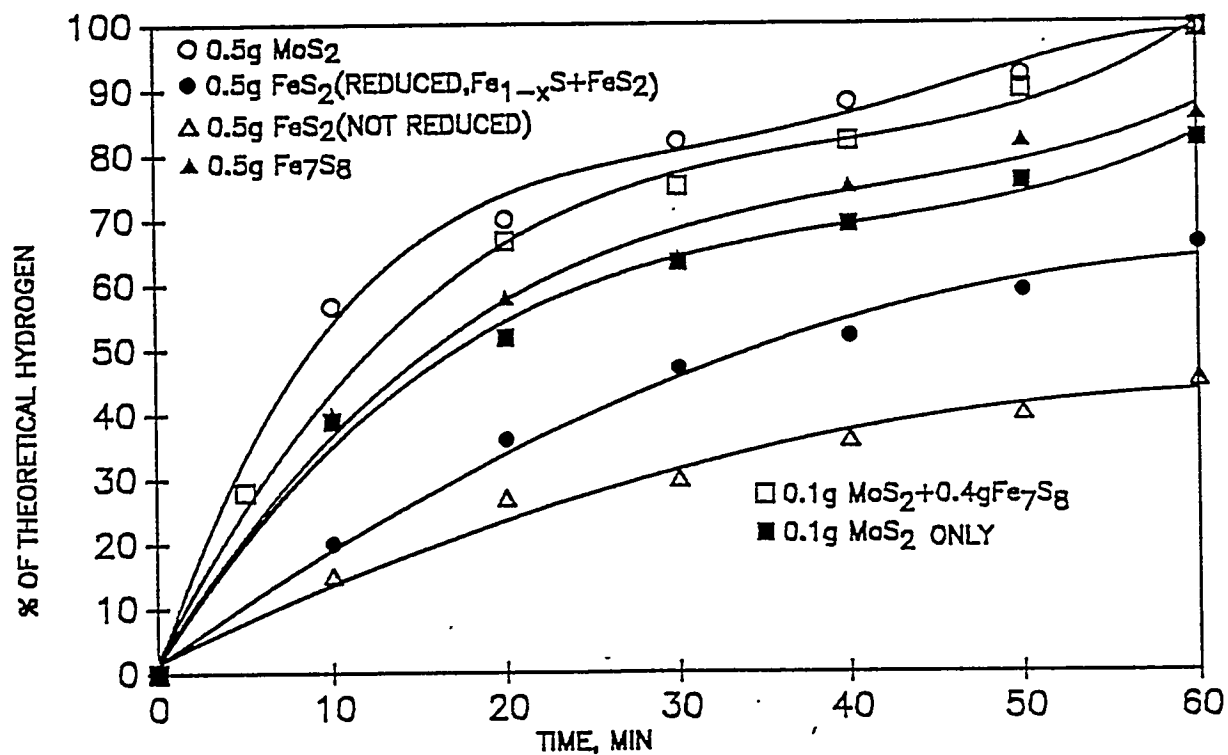


Figure 4. Evolution of molecular hydrogen from 9,10-DHP in presence of DCL catalysts, phenanthridine as vehicle.

TASK IV

Project IV.2

IMPROVED CATALYSTS FOR COAL LIQUEFACTION AND CO-PROCESSING: NEW INITIATIVE IN DISPERSED SLURRY PHASE CATALYSIS

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INTRODUCTION

During the past year, we have studied the catalytic activity of a nanoscale dispersed iron oxyhydroxide catalyst using four coals and several model compounds in a tubing bomb microreactor. Several forms of iron catalyst were examined including the original 3 nm iron oxyhydroxide, H₂ pre-reduced and in-situ sulfided forms. The objective of our research was to examine the effectiveness the dispersed iron catalyst in coal liquefaction and model compound reactions. A variety of coals and process conditions was examined. Model compound reactions were performed using the same catalyst to provide additional insight regarding catalyst performance.

EXPERIMENTAL SECTION

The original catalyst employed in our experiments was a commercial superfine iron oxyhydroxide obtained from Mach-I Inc. Analysis showed the catalyst to be 64 wt% Fe (FeOOH = 63%), with a N₂ BET surface area of 215 m²/g and particle size of 3 nm. Except as noted, the catalyst was used as received without drying, or other pretreatment. Coal liquefaction runs were performed using HVA bituminous Blind Canyon (BC) DECS-17 coal and three Argonne coals, Illinois No. 6 (ILL), Pocahontas No. 3 (POC), and Wyodak (WY). Elemental sulfur was added

as an additional sulfur source for sulfidation of the catalyst. The detailed reaction conditions are shown in Table I. The pentane and tetrahydrofuran insoluble products were determined as an indication of catalyst activity and liquefaction reactivity. Equation 1 was used to calculate the pentane solubles (PS) (including gases) and tetrahydrofuran solubles (THFS) on an maf coal basis.

$$\% \text{ MAF SOLUBLES} = \frac{W_o(1-M) - (IS - W_c)}{W_o(1-A-M)} \cdot 100 \quad (1)$$

- W_o : initial weight of coal as charged to TBMR.
 A : fraction of ash in the coal as charged.
 M : fraction of moisture in the coal as charged.
 IS : weight of insolubles from fractionation procedure, including ash and catalyst.
 W_c : weight of catalyst following reaction.

Model compound reactions chosen were the hydrogenation of naphthalene (NAPH) and biphenyl (BPH) and the hydrocracking of dibenzyl ether (DBE), benzaldehyde (BAH) and benzyl alcohol (BAL). Experiments were carried out in two different types of TBMR at the conditions in Table I. The catalyst reduction process was performed by placing the TBMR in a furnace for 24 hours with a H_2 flow rate of 100 cc/min measured at ambient conditions. For model aromatic ring hydrogenation reactions, an extent of hydrogenation A_H was defined as follows:

$$\text{OR } A_H = \frac{2M_{TET} + 5M_{DEC}}{5(M_{NAPH} + M_{TET} + M_{DEC})} \quad A_H = \frac{3M_{CHB} + 6M_{DCH}}{6(M_{BPH} + M_{CHB} + M_{DCH})} \quad (2)$$

In equation (2), the M_i are the moles of compound i in the reaction products consisting of tetralin (TET) and decalin (DEC) for NAPH hydrogenation and cyclohexylbenzene (CHB) and dicyclohexyl (DCH) for BPH hydrogenation, respectively. For hydrocracking reactions, activity was expressed by the conversion of the original reactant.

Product samples collected were analyzed by gas chromatography using temperature programming to improve peak resolution and decane as an internal standard. Peak identification was made from previous literature results confirmed by standard addition of authentic compounds.

RESULTS AND DISCUSSION

Coal liquefaction experiments were performed in the presence and absence of dispersed iron catalyst using several coals under various reaction conditions including catalyst loading and initial surface area, solvent type, and reaction temperature. BC coal was the baseline coal used in our experiments.

Effect of Catalyst and Sulfur Addition on Blind Canyon Coal. Figure 1 shows the effect of catalyst and sulfur additions on product yields with BC coal at the baseline reaction conditions in Table I. Sulfur alone increased PS by 5% while the iron catalyst alone gave a 7% increase. Combination of sulfur and catalyst increased the PS yield by 11%. The THFS show corresponding although somewhat smaller relative increases in line with the behavior of the PS. It appears that the effect of sulfur and catalyst are approximately additive and that a large degree of synergism is not reflected in the increased yields. To some degree this lack of synergism argues against the necessity of having the iron in the sulfided form, FeS_x ($x \approx 1.05-1.15$), to function catalytically.

Catalyst Activity with Various Solvents. Figure 2 shows a comparison of the results obtained using different liquefaction solvents with BC coal at baseline reaction conditions. Tetralin was used as the baseline solvent. When mineral oil (an aliphatic non-donor) was used in place of tetralin, little difference was obtained between the PS and THFS yields with or without catalyst. The lack of effectiveness of the catalyst with this solvent emphasizes the fact

that a catalytic effect in coal liquefaction is a result of a combination of effects including the solvent, e.g. possibly hydrogen shuttling, in addition to its effect on the coal alone. The results with the aromatic solvent, 1-methylnaphthalene, showed a similar trend as tetralin with regard to the effectiveness of the catalyst. The PS yields with creosote oil were very low in that there was actually an increase in pentane *insolubles* formed during the liquefaction reaction. It is probable that creosote oil undergoes regressive combination reactions with coal radicals. In general, these results affirm that catalytic coal liquefaction must be viewed in light of the *overall* solvent-coal reaction system rather than simply as a catalyst-coal interaction.

Effects of Catalyst Loading and Surface Area. Variations in catalyst loading and surface area were examined using both BC coal and model compounds. As shown in Figure 3, increasing the catalyst loading increases the PS and THFS yields; however the incremental increase is not linear and additional catalytic benefit declines significantly as the loading is increased. Similar results were observed with the model hydrogenation reaction of NAPH in mineral oil as shown in Figure 4, where the extent of hydrogenation defined by equation (2) increased sharply in a very narrow range of catalyst loading to a constant level, corresponding to the complete conversion of NAPH to TET. Figure 5 shows the dependence of product yields on the initial surface area of the catalyst. There is a decrease of PS and THFS with the decrease in catalytic surface area. These results are believed to be caused by sintering of the original 3 nm catalyst particles or by a change in chemical structure.

Liquefaction of Argonne Premium Coals. Figure 6 shows the effect of catalyst addition on liquefaction of three different Argonne coals at both 400°C and 425°C. Also shown is the baseline DECS-17 BC coal. The WY and the ILL coals did not show as significant an increase in PS as did POC, which is a LVB coal. All Argonne coals showed significant increases in THF

solubles in the presence of the catalyst with POC again showing the greatest relative increase. The trend in liquefaction yields evidenced by the Argonne coals is in general agreement with other reported results using these same coals.

Effect of Reaction Temperature. Figure 6 also illustrates the effect of increasing reaction temperature from 400 to 425°C on catalytic liquefaction with the BC and Argonne coals. Generally all coals showed a significant increase in PS and THFS at 425°C as compared to 400°C, however, the coals showed rather different susceptibilities to catalytic vs. thermal action. The contrast in the response of POC as compared to WY and ILL with regard to catalytic vs. thermal actions is particularly striking. POC was greatly affected by catalyst and little influenced by temperature while ILL and WY were primarily responsive to the change in temperature and less affected by the catalyst. On the other hand, BC appears to be about equally affected by catalyst and temperature. The THFS yields of the coals are not quite as definitive as the PS yields regarding catalytic vs. thermal activity, although increases with both temperature and catalyst for all coals are readily apparent.

Model Compound Hydrogenation Reactions. Several forms of dispersed iron catalyst were employed including the original iron oxyhydroxide, H₂ pre-reduced iron and FeS_x. For some experiments the original iron oxyhydroxide was pre-reduced with H₂. To establish a proper pre-reduction procedure, the hydrogenation of NAPH was studied using iron which had been pre-reduced for 24 hours at temperatures of 200 to 600°C. The results in Figure 7 show that reduction temperatures above 250°C are detrimental to the catalyst activity, presumably due to sintering of the catalyst during reduction. Therefore, a reduction temperature of 200°C was chosen for further experiments. Figure 8 shows that, for the hydrogenation of both NAPH and BPH, the pre-reduced iron catalyst gives higher extents of hydrogenation (eq. (2)) than the original oxide form, while

CS₂ addition almost completely poisons both catalysts, whether in the original form or pre-reduced form. These results show that the sulfided form is a *much less active* aromatic ring hydrogenation catalyst than the reduced form. A notable phenomenon observed is that, in both NAPH and BPH reaction systems, significant secondary hydrogenation reactions, i.e., the conversion from tetralin to decalin and from cyclohexylbenzene to dicyclohexyl, took place *only* when the catalyst had been pre-reduced, even when the catalyst loading was increased almost ten times as shown for NAPH hydrogenation in Figure 4. This observation suggests that the greater aromatic ring hydrogenation activity of reduced iron is due to largely catalytic sites of greater activity rather than merely an increase in number of sites. Moreover, it is likely that when the original oxyhydroxide catalyst is used in the complete absence of sulfur, a partial in-situ reduction occurs and the active sites are a reduced iron phase.

Model Compound Hydrocracking Reactions. DBE and the related model compounds, benzaldehyde (BAH) and benzyl alcohol (BAL) were used as initial reactants to examine the activity and selectivity of the dispersed iron catalyst in this work. Figure 9 shows the conversions of DBE, BAH and BAL with and without catalyst at 300°C. All of the iron catalysts catalyzed the cracking of DBE, particularly the reduced iron and iron sulfide which had approximately the same activities. This is in marked contrast to the NAPH and BPH aromatic hydrogenation reactions where the reduced iron had much greater activity. In the presence of catalyst, toluene was always the dominant cracking product of DBE, while BAH and BAL were detected only in trace level. When BAH was used as initial reactant in the absence of any catalyst, benzoic acid (BZA) was found to be the major product. When the catalyst was employed, however, primary products were TOL and BAL with the concentration of BZA being greatly reduced. The evidence that TOL was found to be always the dominant cracking product in all of the three reaction

systems in the presence of catalyst implies that the iron catalysts generally promote the complete cleavage of the C=O bond in BAH and the C-O bond in BAL and DBE. Reduced iron and iron sulfide had almost the same activities for the cracking of DBE and BAL, while reduced iron showed superior activity to iron sulfide for the cracking of BAH. In additional model compound reactions carried out in this work, no significant catalytic cracking was observed when applying the same catalysts to the reaction systems of biphenyl, diphenylmethane and isopropylnaphthalene at 400°C and 7.9 MPa H₂ (cold) where the cracking of C_{ar}-C_{ar} or C_{ar}-C_{alk} bonds was required.

Table I. Baseline Reaction Conditions for Coal and Model Compound Experiments

TBMR Type ^a	A	A (B)	A (B)	A (B)
Reactant wt., g	Coal 3	NAPH 0.12 (0.24)	BPH 0.12 (0.24)	DBE,BAH & BAL 0.12 (0.24)
Catalyst wt., g	0.06	0.03 (0.06)	0.03 (0.06)	0.03 (0.06)
Solvent wt., g	Tetralin 10	Mineral Oil 6 (12)	Hexadecane 6 (12)	Cyclohexane 6 (12)
Sulfur Source wt., g	Elementary Sulfur 0.1	CS ₂ 0.012 (0.024)	CS ₂ 0.012 (0.024)	CS ₂ 0.012 (0.024)
Temp., °C	400	350	300	300
H ₂ Pressure ^b , MPa	8.6	7.9	7.9	7.9
Time, h	1	1	1	1

^a The volume of Type A was 45 cc for coal runs and 17 cc for model compound runs. Type B is the same as Type A (45cc) except modified to have both inlet and outlet ports. This type TBMR was used for catalyst pre-reduction with H₂.

^b Measured at ambient temperature.

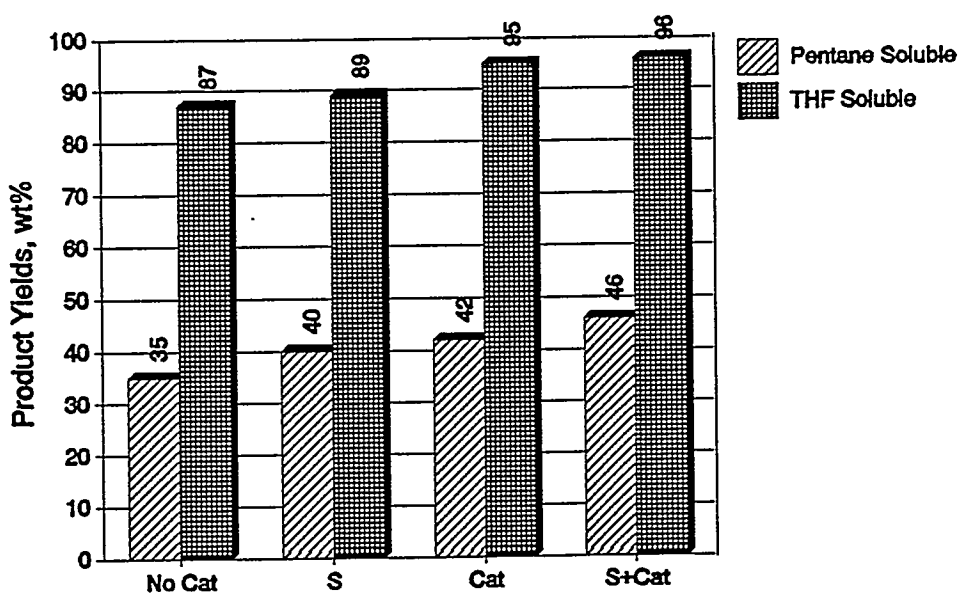


Figure 1 Effect of catalyst and sulfur addition on pentane and tetrahydrofuran soluble yields with Blind Canyon coal

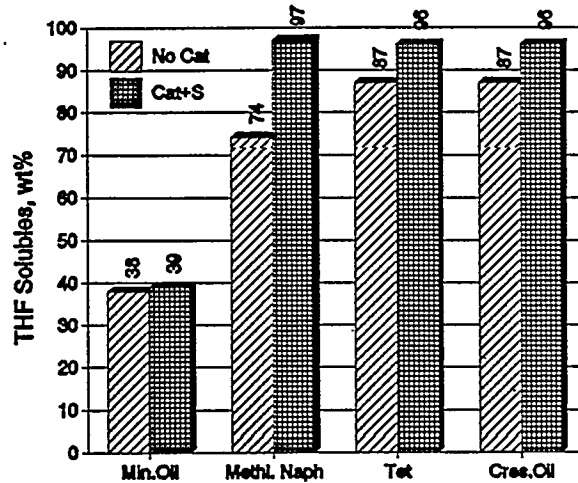
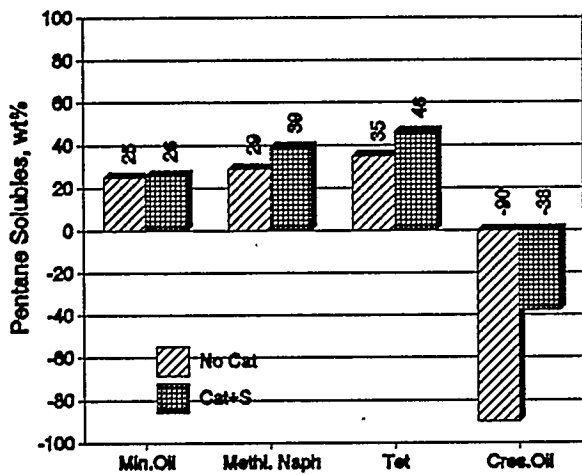


Figure 2. Catalyst performance using Blind Canyon coal with different types of liquefaction solvents.

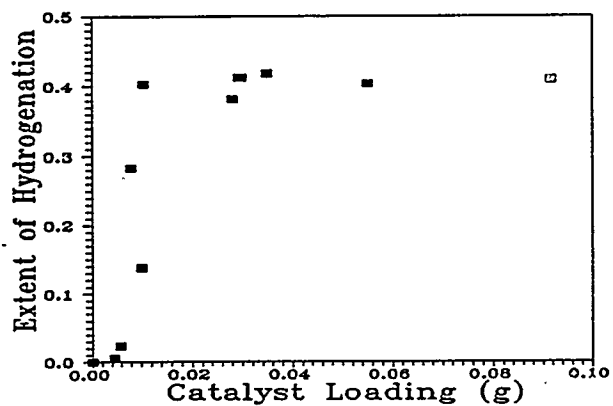
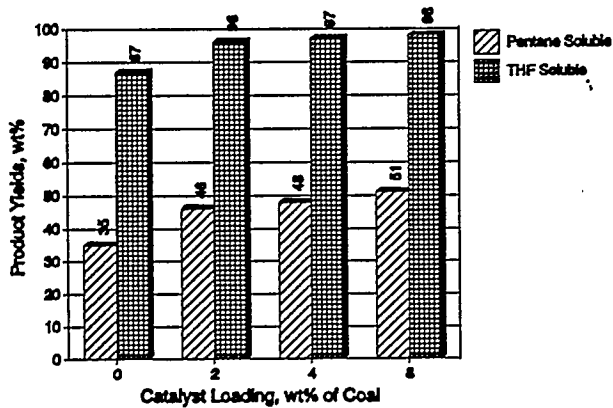


Figure 3. Variation in pentane and tetrahydrofuran soluble yields with catalyst loading

Figure 4. Effect of catalyst loading on extent of naphthalene hydrogenation at 350°C.

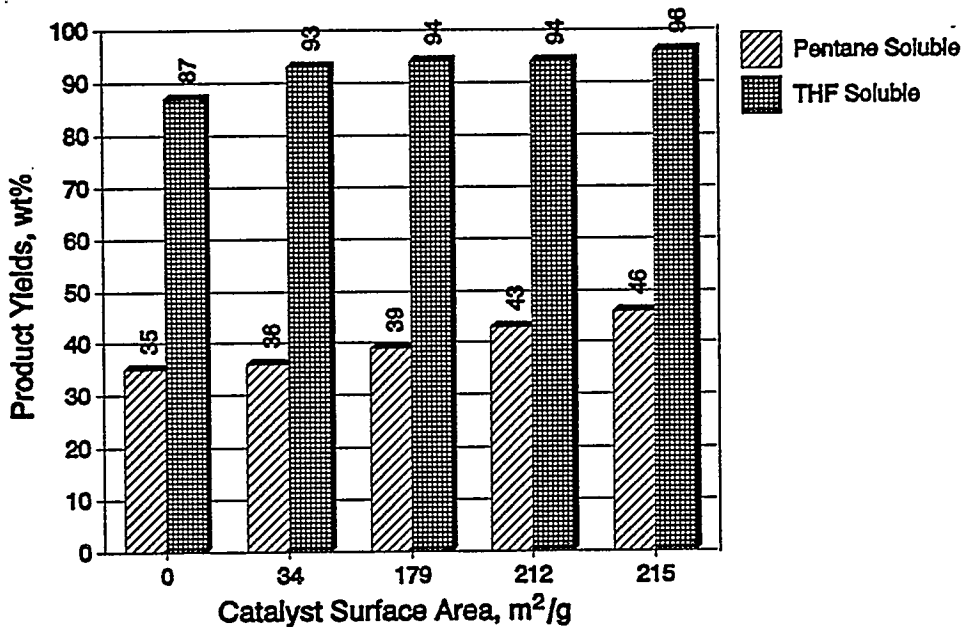


Figure 5. Variation in pentane and tetrahydrofuran soluble yields as a function of initial catalyst surface area at constant loading of 2 wt% of coal.

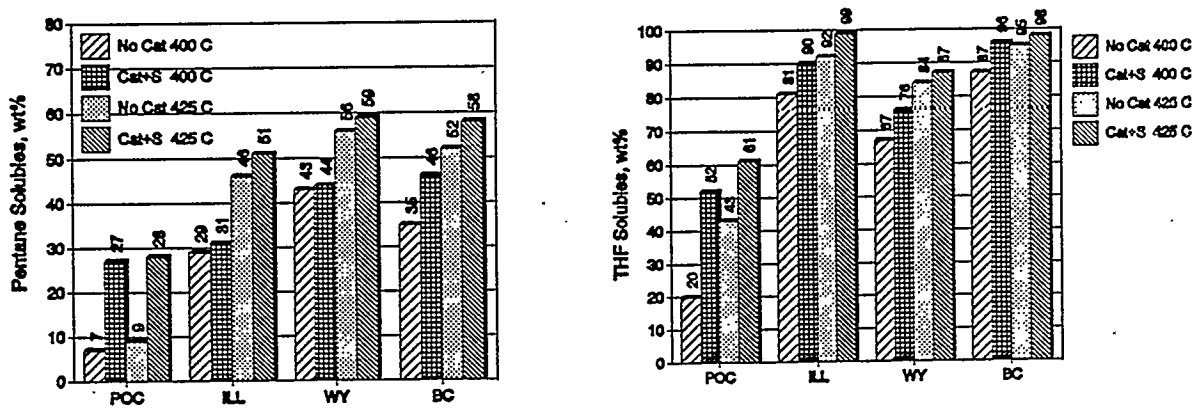


Figure 6. Comparison of catalytic and non-catalytic liquefaction yields with BC and Argonne coals at 400°C and 425°C.

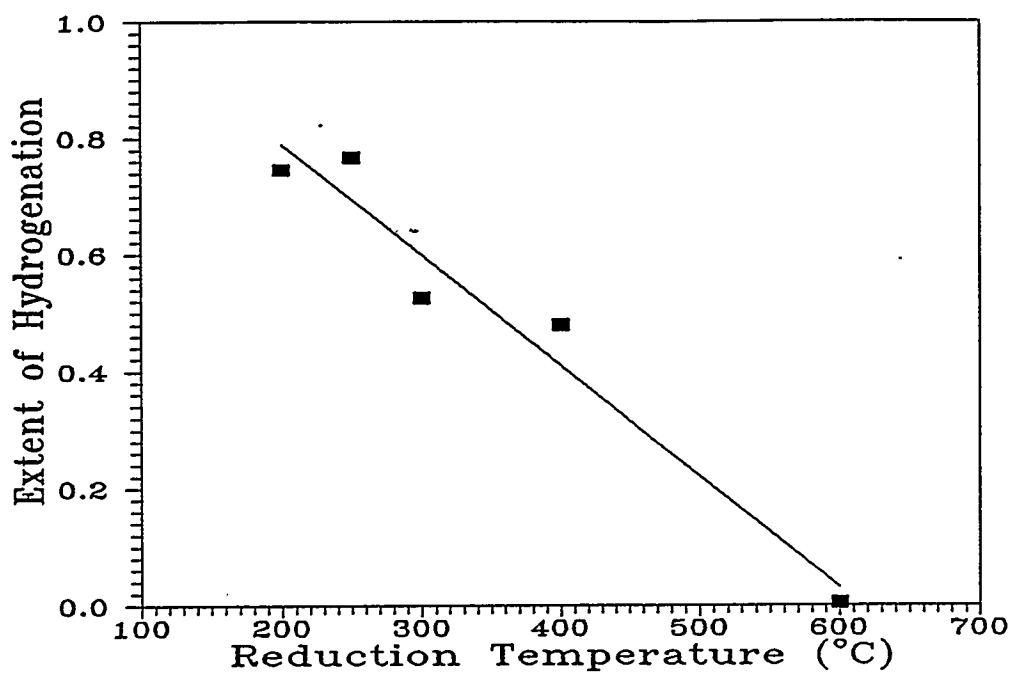


Figure 7. Effect of reduction temperature of catalyst on extent of naphthalene hydrogenation.

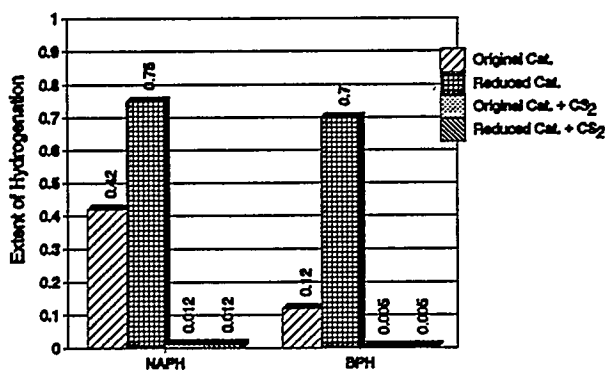


Figure 8. Effect of catalyst on extent of naphthalene and biphenyl hydrogenation at 350°C and 300°C, respectively.

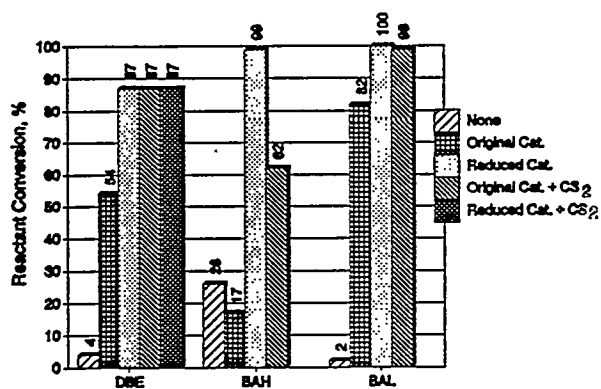


Figure 9. Effect of catalyst on hydrocracking of dibenzyl ether, benzaldehyde and benzyl alcohol at 300°C.