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Technical Progress Report
July - September 1995

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Chunshan Song, Eckhardt Schmidt and Harold H. Schobert

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DISCLAIMER

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ABSTRACT

Coal liquefaction involves cleavage of methylene, dimethylene and ether bridges connecting polycyclic aromatic units and the reactions of various oxygen functional groups. Here in this quarterly, we report on the hydrocracking of 4-(1-naphthylmethyl)bibenzyl in the presence of iron (Fe) catalysts and sulfur and residual wall catalytic effect.

Catalytic hydrocracking of 4-(1-naphthylmethyl)bibenzyl (NMBB) predominantly yielded naphthalene and 4-methylbibenzyl. Various iron compounds were examined as catalyst precursors. Sulfur addition to most catalyst precursors led to substantially higher catalyst activity and higher conversion. NMBB was also treated with sulfur in the absence of iron compounds, in concentrations of 1.2–3.4 wt%, corresponding to the conditions present in reactions with added iron compounds. Increasing sulfur concentrations led to higher NMBB conversions. Furthermore, sulfur had a permanent effect on the reactor walls. A black sulfide layer formed on the surface which could not be removed mechanically. The supposed non-catalytic reactions done in the same reactor but after experiments with added sulfur showed higher conversions than comparable experiments done in new reactors. This wall catalytic effect can be reduced by treating the sulfided reactors with hydrochloric acid. The results of this work demonstrate the significant effect of sulfur addition and sulfur-induced residual wall effects on carbon-carbon bond cleavage and hydrogenation of aromatics.

Technical Progress

Hydrocracking of 4-(1-Naphthylmethyl)bibenzyl in the Presence of Iron Catalysts and Sulfur and Residual Wall Catalytic Effect

Introduction

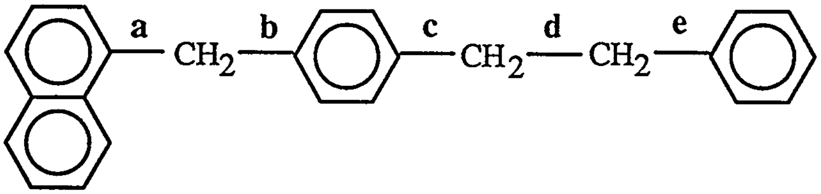
Direct coal liquefaction is facilitated by use of catalysts, to aid in the initial depolymerization of the coal macromolecule or in the hydrotreatment of the primary products of reaction, or both. Over the years compounds of virtually every element that might be suspected of possessing catalytic activity have been tested as potential liquefaction catalysts. Iron compounds often appear to be less active than compounds of some other elements, notably molybdenum, when tested under comparable conditions. Despite that, a variety of reasons indicate that iron-based catalysts offer many advantages for liquefaction processing. These advantages include low cost; ready availability; the potential of use as "once through" catalysts, obviating the need for catalyst recovery and recycle operations; and reduced environmental concerns on disposal. As a result, the past decade has witnessed an extraordinary research effort on iron-based catalysts for direct liquefaction.

The intervention of the catalyst in the early stages of coal decomposition and dissolution is likely to be facilitated if the catalyst is well dispersed over the surface of the coal particles. Catalyst activity may also depend on particle size. The substance generally considered to be the most active iron-based liquefaction catalyst is the non-stoichiometric sulfide pyrrhotite, $Fe_{1-x}S$.[1] Many iron-containing materials have been tested as catalysts, including red mud,[2-4] iron(III) oxide[5,6] and aerosols of iron oxides,[7] iron(III) oxy-hydroxide,[5,8] sulfated iron (III) oxide,[5,9,10] sulfated iron(III) oxyhydroxide,[8] and a variety of other oxide and hydrous oxide phases.[11] Since the iron oxides and sulfides are not soluble in common solvents, possibly making it hard to achieve a good dispersion of small particles, so-called catalyst precursors can be used instead. A catalyst precursor is a compound that may not possess much, if any, catalytic activity itself, but transforms to an active catalyst under the reaction conditions of interest. A remarkable variety of iron compounds has been evaluated in recent years as prospective catalyst precursors. These include iron(III) nitrate,[12,13] iron(II) sulfate,[2,4,13,14] iron(III) sulfate,[13] iron(III) chloride,[15] iron(II) oxalate,[16] iron(III) acetate,[17] iron(III) acetylacetonate,[16,18] iron(II) naphthenate,[18] iron(II) stearate,[18] iron pentacarbonyl,[3,10,16,19,20] triphenylphosphine-substituted iron carbonyls,[21] and various binuclear organometallics[22,23] such as $(C_5H_5)_2Fe_2(CO)_4$ and (μ-

$S_2)Fe_2(CO)_6$. An ingenious effort has also been made to use an iron-loaded coal as a catalyst for reactions with untreated coals.[20]

It has been known for some time that iron oxides are not as effective in catalyzing hydrogenolysis reactions as iron sulfides.[24] Thus when iron compounds not containing sulfur are used as catalysts or catalyst precursors, attempts are made to sulfide the material before use. Elemental sulfur serves as a sulfiding agent.[6,25,26] Other sulfur compounds also work in this application; sodium sulfide is an example.[2,15] A useful review of the phase relationships in the Fe–O–S system is available.[27] Iron sulfide in combination with hydrogen sulfide as liquefaction catalyst has also been reviewed.[28]

Because coals have ill-defined structures and reactions of coals can lead to large numbers of products even under mild conditons, fundamental work in coal chemistry has customarily relied on the use of model compounds. These materials have known structures and, ideally, their reactions lead to a small number of products. This simplifies both the analyses of the products and attempts to understand reaction mechanisms or pathways. Recently 4-(1-naphthylmethyl)bibenzyl (NMBB) has become a popular model compound for studying coal-like reactions, particularly under liquefaction conditions.[4,5,11,18,21,29-33] The structure of NMBB is



An intriguing feature of the NMBB structure is the presence of five different C_{ar}-C_{al} or C_{al}–C_{al} bonds. Following the system established by earlier workers, these bonds are denoted as **a** through **e** in the structure shown above. (Some authors refer to this compound as naphthylbibenzylmethane and use the abbreviation NBBM; the system of labeling the bonds remains the same.)

Experimental Section

Materials. NMBB was purchased from TCI America. A sample of superfine iron oxide (SFIO) was provided by Mach I, Inc., King of Prussia, Pennsylvania. All other compounds—iron catalyst precursors, solvents and sulfur—used in this study were purchased from commercial sources and were used without further treatment or purification.

Reaction Conditions. Reactions were conducted in 33 mL 316-stainless steel microautoclaves (tubing bombs) at 400°C for 30 min (in the fluidized sandbath). The reaction time of 30 min includes the reactor heat-up time of about 6 min. In a typical experiment, the reactor was loaded with 0.78 mmol NMBB, a given amount of catalyst precursor (2.11 wt% Fe, based on NMBB), and 0.78 mmol n-tridecane solvent. The reactor was purged three times with hydrogen and then pressurized with hydrogen to 6.9 MPa at ambient temperature. A preheated fluidized sand bath was used as the heat source. The horizontal reactor was agitated vertically at ≈240 cycles/min to provide mixing. After the reaction, the hot reactor was quenched in cold water. The liquid products were washed from the reactor with 15 mL dichloromethane through a filter paper for subsequent analysis of the filtrate. The reactors were cleaned by treating in a base bath (KOH in aqueous isopropanol), followed by water and ethanol washing and drying prior to the subsequent reaction.

Analyses. The products were identified by gas chromatography / mass spectrometry (GC/MS) using a Hewlett-Packard model 5890 II GC coupled with a Hewlett-Packard model 5971A mass selective detector operating in the electron-impact mode at 70 eV. The column was a 30 m long, 0.25 mm diameter J&W type DB-17 column coated with 50% phenyl–50% methylpolysiloxane at a thickness of 0.25 µm. For quantification of the products, a Hewlett-Packard model 5890 II GC was used, with the same DB-17 column and a flame ionization detector. Both GC and GC/MS were temperature-programmed from 40 to 280°C at 4°C/min with a final holding time of 15 min. The response factors for ten of the products were determined using pure compounds. Because of the small amount (250 mg) and high molecular weight of NMBB used for reaction, its recovery was not always satisfactory. Conversions were determined by summing the amounts of reaction products recovered.

Results and Discussion

Baseline Reaction without Iron Catalyst or Sulfur Addition. Reaction of NMBB without added catalyst provides a baseline for comparison of all of the catalytic reactions. Results are shown in Table 1. Naphthalene and 4-methylbibenzyl are the main products. They arise from hydrocracking at bond a. A small amount of tetralin forms, indicating that even in the absence of catalyst, some utilization of gaseous hydrogen occurs. The low conversion observed in this reaction, 3.9%, agrees well with other reported values in the literature.[18,29,30] A temperature of 400°C seems to be the threshold needed for thermal reactions of NMBB, since it does not thermally react at temperatures <400°C.[31] Previous investigators have reported cleavage at bond **a**, as indicated, for example, by identification of 4-methylbibenzyl among the reaction products.[18,29,30] However, it has also been reported that, at least for temperatures ≥410°C the dominant cleavage in thermal runs is at bond **d**.[29,30] Cleavage at this site would explain the observed formation of naphthyltolylmethane as a product.[18] While our results from catalytic reactions support the pathway via bond **a**, we also found naphthyltolylmethane as a product in non-catalytic reactions at 400°C for 30 min (Table 1) or 60 min. Naphthyltolylmethane is believed to be formed via non-catalytic cleavage of bond **d**. Such a product was not found in catalytic reactions. We have no evidence from any of our reactions for extensive demethylation accompanying the hydrogenolysis of NMBB.

Effects of Iron-Containing Precursors on Hydrocracking of NMBB. Several iron-containing catalyst precursors—ferrocene, iron(II) sulfate, and SFIO—were tested to study the impact of sulfur addition on the catalytic reactions of NMBB with hydrogen at 400°C. To establish a baseline for evaluating the effect of added sulfur, control reactions were performed in the absence of sulfur. Results are shown in Table 1. It should be noted that the conversion values reported here are based on the mass of recovered products, and may be lower than true values. The true NMBB conversion values should be ≥ sum of molar yields of naphthalene, methylnaphthalene, tetralin, naphthyltolylmethane, benzylnaphthalene (if any), and tetrahydro-NMBB because these products correspond to the starting material in a stoichmetric (molar) ratio of 1:1. The runs reported in Table 1 with or without added sulfur were conducted using the reactors that have not been exposed to sulfur. The effect of added sulfur without Fe and the influence of residual wall catalytic effect of the "sulfided reactors" are discussed later in this report.

In terms of NMBB conversion, the order of catalyst activities was SFIO > ferrocene >> iron(II) sulfate. Although the observed activities differed in each case, in all three reactions naphthalene and 4-methylbibenzyl dominated the product slate. Under these conditions, bond **a** was the preferred site for hydrocracking. Toluene, produced likely by cleavage of bond **d**, and bibenzyl, from cleavage of bond **b**, represented minor products in these reactions. Reaction in the presence of ferrocene showed formation of some methylnaphthalene, the other product from cleavage of bond **b**.

These results agree with previous observations. Iron-catalyzed reactions appear to show high selectivity for cleavage of bond **a**,[5] with naphthalene and 4-methylbibenzyl consistently being major products.[11] In iron-catalyzed reactions, cleavage of bond **b** is limited.[5] Reaction at site **d** appears unaffected by added catalyst, the products from cleavage at **d** being in about the same amount from catalytic or non-catalytic reactions.[5,21] The apparent resistance of the weak bond **d** to cleavage in these reactions derives from the fact that nonstoichiometric iron sulfides are very selective for cleavage of C_{ar}–C_{al} bonds, particularly between polycyclic aromatic systems and aliphatic carbon atoms, even in the presence of weak C_{al}–C_{al} bonds.[5] Supporting evidence comes from reactions of 1,2-dinaphthylethane, in which ring hydrogenation was favored relative to cleavage of the C_{al}–C_{al} bond.[34]

In the reactions with ferrocene and SFIO, tetralin appeared as a minor product. Tetralin would arise from hydrogenation of naphthalene. Its formation shows that the hydrocracking reactions were accompanied by some hydrogenation, though under these conditions hydrocracking dominates. The hydrogenation activity of the three catalyst precursors, deduced from the amount of tetralin formed, is SFIO > ferrocene > iron(II) sulfate. This parallels the order of activity for conversion of NMBB. The small contribution of tetralin to the product slate is consistent with iron sulfides having low activity for hydrogenation of aromatic rings.[1] For example, iron sulfides are much less effective at ring hydrogenation than is metallic iron.[35] No evidence was observed for hydrogenation of any of the reaction products with single aromatic rings. This is consistent with the general observation of naphthalene rings being more easily reduced than benzene rings (at least for reduction to tetralin).[36,37] The hydrocracking of naphthalene proceeds via reduction to tetralin, followed by isomerization to methylindan, and subsequent bond cleavage in the reduced ring.[38] We found no evidence for indans among the reaction products, suggesting that, even had longer reaction times been employed, naphthalene hydrocracking is unimportant in these systems.

Comparison of the products of non-catalytic reaction and reaction in the presence of iron(II) sulfate shows that, even though the conversions are similar, the addition of the iron(II) sulfate has affected the product distribution. With added iron(II) sulfate, reaction occurs dominantly at bond **a**, forming naphthalene and 4-methylbibenzyl, and to a lesser extent at bond **b**, to form bibenzyl. No other bonds appear to be affected in the reaction with iron(II) sulfate under these conditions. The non-catalytic reaction, at the same level of conversion, shows hydrocracking at bonds **a** and **d**. These results demonstrate that the added iron(II) sulfate intervenes by affecting the hydrocracking pathways at the molecular level, even though it has no macroscopic effect in terms of enhancing conversion. Essentially, iron(II) sulfate shuts down the reaction pathway via bond **d**, and turns on a new pathway via bond **b**. A further point of difference lies in the utilization of gaseous hydrogen; some hydrogenation product (tetralin) forms in the non-catalytic reaction, but, interestingly, none in the reaction with added iron(II) sulfate.

Experiments using SFIO yielded only moderate conversion (27.1%), even at 400°C. Hydrocracking at bond **a** is the dominant reaction pathway. Hydrogenation of naphthalene ring occurs in this case, giving 7.3% tetrahydro-NMBB. Cleavage of bond **d** occurs to a limited extent, as shown by formation of some toluene. This was not observed in reactions with iron(II) sulfate, which gave much lower conversion. It seems to agree with the general concept that as one uses a more active catalyst, the catalyst itself is less selective in its action.[39]

The addition of sulfur to reactions with added iron compounds gives results markedly dependent on the specific iron compound used in the reaction. The most significant enhancement of conversion was obtained in reactions of SFIO with added sulfur. Compared to reaction without sulfur, the conversion jumps by 51 percentage units, from 27.1% to 78.2% (Table 1). As was the case without sulfur addition, naphthalene and 4-methylbibenzyl dominate the product slate, showing that hydrocracking at bond **a** occurs in greatest extent. Toluene again appears as a minor product, from cracking at **d**. Methylnaphthalene and bibenzyl are minor products from scission of bond **b**. Tetralin remains a minor product, showing that even when the conversion has nearly tripled relative to reaction without added sulfur, hydrocracking is much more important than hydrogenation. in this case, yield of tetrahydro-NMBB (5.5%) is slightly higher than that of tetralin (4.0%). 2-Methylnaphthalene also occurs among the products. It could be formed from the cleavage at the bond b in 4-(2-naphthylmethyl)bibenzyl, which has been observed in a very small amount in the reaction system.[40] 2-Methylnaphthalene could also be formed from isomerization of 1-methylnaphthalene.

The addition of sulfur also enhances conversions obtained with added iron(II) sulfate, although conversion even with added sulfur, 23.9%, is less than that obtained with SFIO and no added sulfur. As in the case of SFIO+sulfur, reaction with iron(II) sulfate and sulfur show the clear dominance of hydrocracking at bond **a**. In fact, the product slates from SFIO+sulfur and iron(II) sulfate + sulfur are generally similar. The most notable difference is the lack of evidence for isomerization (i.e., formation of 2-methylnaphthalene) in the iron(II) sulfate + sulfur system. In contrast to reaction without added sulfur, a small amount of hydrogenation (formation of tetralin) takes place in the iron(II) sulfate + sulfur reactions.

When ferrocene is used as the catalyst precursor, the addition of sulfur actually depresses the conversion. The conversion dropped from 15.8% to 9.6%. Although we do not yet have a good explanation for this behavior, it is not an isolated instance of the unusual effects of organometallic catalyst precursors, particularly those containing the cyclopentadienyl ligand. We also observed a decrease in NMBB conversion upon sulfur addition to cyclopentadienyl diiron tetracarbonyl, $Cp_2Fe_2(CO)_4$ (where Cp = cyclopentadi-enyl).[41] In a related paper, we show the effects of using the bimetallic thiocubane-type precursor $Cp_2Co_2Mo_2(CO)_2S_4$ for hydrotreatment of dibenzothiophene.[42] At comparable catalyst loadings, conversions of dibenzothiophene with this thiocubane were lower, by factors of 2–6, than those obtained with all other molybdenum-containing catalyst precursors tested.

Effects of Sulfur Addition Without Iron Catalysts. Table 2 summarizes results obtained for the addition of sulfur to NMBB reactions but without iron compounds being added. Conversion of NMBB clearly depends on the level of sulfur addition. At 1.2 wt% (based on

NMBB) sulfur, the conversion, 26.1 wt%, compares well to those obtained in reactions with SFIO and with iron(II) sulfate + sulfur, which were 27.1 and 23.9 wt%, respectively. 4-Methylbibenzyl and naphthalene dominate the product slate, again demonstrating high selectivity for NMBB cleavage at bond **a**. These were also the dominant products with the SFIO and iron(II) sulfate + sulfur systems.

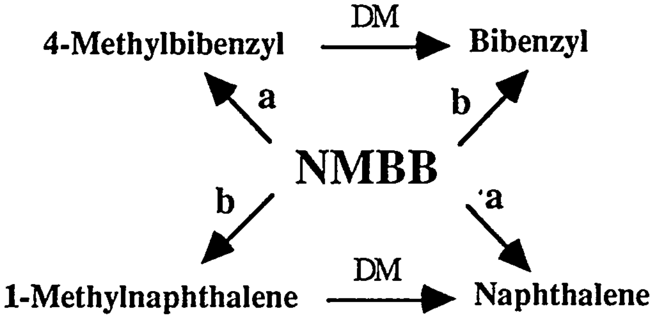
It should be noted that significant amounts of benzothiophene- type sulfur-containing compounds were observed by Darab et al.[43] in the reaction of NMBB in the presence of sulfur with and without an iron catalyst. However, we have confirmed from our GC and GC-MS data that such sulfur compounds, if any, were negligible under the conditions employed. The possible reason for this discrepancy could be that the sulfur/NMBB mol ratio used in the work of Darab et al.[43] is much higher (0.31 mmol S/0.08 mmol NMBB= 3.91) than those used in the present work (0.094 mmol sulfur/0.78 mmol NMBB =0.12 corresponding to 1.2 wt% sulfur added; 0.27 mmol sulfur/0.78 mmol NMBB=0.34 corresponding to 3.4 wt% sulfur added).

Addition of 3.4 wt% sulfur provides 82.5% conversion, the highest observed in any of the tests reported in this report. Naphthalene is the major product. In other reactions, the mol% of naphthalene and 4-methylbibenzyl are roughly comparable, as would be expected from formation of these two compounds via scission of bond **a**. Reaction in the SFIO + sulfur system, which gives almost the same level of conversion (78.2%) provides a good example of this, where naphthalene and 4-methylbibenzyl are 64.1 and 59.6 mol%, respectively. However, in the reaction with 3.4 wt% added sulfur, the similar concentrations of these two products no longer holds, with 74.4 mol% naphthalene but only 32.3 mol% 4-methylbibenzyl.

This discrepancy suggests that secondary reactions may be responsible for the observed product distribution. Two alternatives can be considered: Scission at bond **a** followed by demethylation of the 4-methylbibenzyl would leave naphthalene as one major product, and a mixture of 4-methylbibenzyl and bibenzyl as other major products. Scission at bond **b** would produce bibenzyl and 1-methylnaphthalene; a subsequent demethylation of the 1-methylnaphthalene would form the observed naphthalene. Indeed, the methyl group in 1-methylnaphthalene is somewhat labile, as indicated by the facile isomerization to 2-methylnaphthalene, a product observed only at high levels of conversion. However, the reaction pathway NMBB → bibenzyl + 1-methylnaphthalene → naphthalene could not easily account for the formation of significant amounts of 4-methylbibenzyl, which is indeed observed among the products, at 32.3 mol%. It would be necessary to invoke a transalkylation reaction of 1-methylnaphthalene and bibenzyl that would that would be selective for monomethylation at the 4-position of bibenzyl. It seems that the first alternative, NMBB → naphthalene + 4-methylbibenzyl → bibenzyl, is the more likely.

It should be noted that, unlike in other reaction systems, cleavage of both bond **a** and bond **b** is equally important in the reaction with 3.4 wt% sulfur. Two of the resulting products seem to undergo significant secondary reactions, as shown in Scheme I. (In other words, sulfur-induced bond cleavage of C_{ar}–C_{al} is not as selective as cleavage induced by the iron sulfide catalysts.) Some of the naphthalene may be formed from 1-methylnaphthalene, and some of the bibenzyl may be from 4-methylbibenzyl. At present we do not have enough evidence to specify quantitatively the contribution from the two secondary demethylation reactions.

Scheme I.



Reactions in Sulfided Reactors. When conducting the reactions with added sulfur, we observed that sulfur appears to have a permanent effect on the stainless steel reactor walls, as can be from Table 2. Even new reactors turn black inside after reaction with sulfur, depending on the sulfur concentration. We did not conduct a detailed study of the sulfidation process itself, nor an analysis of the products. A useful review of sulfidation of stainless steels (and other alloys) is available.[44] Sulfidation can be a problem in refinery vessels.[45] Sulfur vapor readily attacks stainless steels above 444°C.[46] In some cases, an outer layer of the corrosion deposit has a composition $Fe_{1-x}S$, similar to that of pyrrhotite.[44] The catalytic properties of reactor walls in coal tar processing has been known for some time.[25,47]Although it is reported that sulfide scales are not as adherent to stainless steels as are oxide scales,[46] in our experiments the black sulfide layer could not be removed mechanically from the reactor walls. The black layer was not removed by treatment with potassium hydroxide in aqueous isopropanol for up to three days. Conversion of NMBB in a sulfided reactor was 23.0 wt% (Table 2), comparable to the 23.9 wt% observed with iron(II) sulfate + sulfur. Once again the major products resulted from scission of bond **a**, being naphthalene and 4-methylbibenzyl. For comparison, the non-catalytic reaction in a new reactor showed a conversion of 3.9 wt%, with cleavage at both bonds **a** and **c** being important. This apparent wall effect could be reduced by immersing a sulfided reactor in 6*N* hydrochloric acid for 5 min. Conversion was halved, to 11.6 wt% (Table 2) with no effect on the principal reaction pathway. We postulate that longer treatment in HCl would completely remove the catalytic sulfide scale and once more provide "non-catalytic" conversions of ≈5%. However, because of the well-known susceptibility of stainless steels to stress corrosion cracking in chloride environments,[46] we did not wish to compromise the mechanical integrity of the reactors and did not conduct a more severe reaction in HCl.

To test whether the apparent catalytic effect of sulfided reactor walls was indeed an effect of the walls, or was an artifact of elemental sulfur trapped in the reactor, we washed sulfided reactors with chloroform and ethanol to remove any material trapped in the upper stem of the reactors. Experiments performed after this treatment showed no difference compared to reactions done without washing the reactor. The wall effect does indeed seem to be due to the formation of a sulfide layer on the reactor walls.

Summary and Conclusions

A variety of iron compounds catalyze the hydrogenolysis of NMBB. For most, but not all, of these compounds, the conversion is significantly enhanced by the addition of sulfur to the reactor. In fact, the conversion of NMBB can also be enhanced by the addition of sulfur itself, even in the absence of any additional iron compound. The conversions observed in "sulfur only" reactions depend on the specific level of sulfur addition used. Sulfiding the reactor walls also serves to enhance conversion; the effect of the sulfide layer on the walls can be reduced by treatment in 6*N* hydrochloric acid. We presume that a sufficiently vigorous acid attack could eventually destroy the catalytic effect of the sulfided walls completely, and remove any wall effect.

All of the reactions result in the production of naphthalene and 4-methylbibenzyl as the major products. These compounds arise from cleavage of NMBB at bond **a**. Hydrogenation of NMBB itself or of the primary reaction products is a minor process under our reaction conditions (400°C, 6.9 MPa H_2 cold, 30 min.). The addition of 3.4 wt% sulfur enhances a second reaction pathway, leading to bibenzyl and methylnaphthalene via bond **b**.

Ferrocene behaved differently than superfine iron oxide or iron(II) sulfate, in that conversions in ferrocene + sulfur reactions actually dropped relative to reactions without sulfur. We have not yet determined the reason for this behavior, but find that it is consistent with other systems in which sulfur is added with cyclopentadienyl-containing catalyst precursors.[41,42]

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40 An anonymous reviewer has kindly provided the published information that their group and others have seen 4-(2-naphthylmethyl)bibenzyl, up to 4% of the original 4-(1-naphthylmethyl)bibenzyl. We do not know whether these two NMBB isomers co-elute on the GC column used in this work, but we analyzed one batch of the NMBB samples purchased from TCI America and found only one NMBB peak by GC-MS and GC. We can not rule out the possibility that 4-(2-naphthylmethyl)bibenzyl may be formed from isomerization of 4-(1-naphthylmethyl)bibenzyl under the reaction conditions.

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Table 1. Effect of Fe Catalyst Precursors on Hydrocracking of NMBB at 400°C

Catalyst Precursor[a]	None	Cp_2Fe	Cp_2Fe+S	$FeSO_4x7H_2O$	$FeSO_4x7H_2O$ +S	Superfine Fe_2O_3	Superfine Fe_2O_3+S
Conversion (wt%)[b]	3.9	15.8	9.6	3.7	23.9	27.1	78.2
Product (mol %)[c]							
Toluene	1.0	1.6	1.1		1.3	1.3	1.9
p-Xylene						0.3	0.7
Tetralin	0.6	0.4	0.3		0.6	3.0	4.0
Naphthalene	1.4	13.8	10.3	4.5	24.0	16.4	64.1
1-Methylnaphthalene		5.6	0.5		1.5		5.8
2-Methylnaphthalene							1.4
Bibenzyl		2.6	0.6	0.6	2.5	1.0	8.9
4-Methylbibenzyl	2.0	9.4	7.4	2.6	19.1	17.4	59.6
NTM[d]	1.2						
Tetrahydro-NMBB						7.3	5.5

a) When sulfur was added, the atomic ratio of S:Fe was 1:1.
b) Conversion is the sum of yields of recovered products expressed in wt%.
c) Mol% based on the starting material, NMBB.
d) Naphthyltolylmethane

Table 2. Effect of Sulfur Addition on Hydrocracking of NMBB at 400°C without Fe Catalysts

Sulfur Addition	None	1.2 wt% S	3.4 wt% S	None	None
Reactor History	Unsulfided reactor[a]	Unsulfided reactor[a]	Unsulfided reactor[a]	Sulfided reactor[b]	HCl treated reactor[c]
Conversion (%)	3.9	26.1	82.5	23.0	11.6
Product (mol %)					
Toluene	1.0	1.4	4.9	1.0	1.0
Tetralin	0.6	0.8	2.9	0.8	0.4
Naphthalene	1.4	24.8	74.4	19.1	10.8
1-Methylnaphthalene		1.7	9.5	0.8	0.7
2-Methylnaphthalene			7.8		
2-Methyltetralin			0.4		
NTM[b]	1.2				
Bibenzyl		2.4	42.5	1.0	1.2
4-Methylbibenzyl	2.0	22.1	32.3	18.3	9.7
TH-NMBB				2.7	

a) Unsulfided reactor refers to the reactor that was used in previous experiments without added sulfur.
b) Sulfided reactor refers to the reactor that was used in a previous experiment with 3.4 wt% added sulfur.
c) HCl treatment was performed on the sulfided reactor at room temperature.