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**Novel Bimetallic Dispersed Catalysts for
Temperature-Programmed Coal Liquefaction**

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**Technical Progress Report
January - March 1996**

(Approved)

Chunshan Song, Eckhardt Schmidt and Harold H. Schobert

**Fuel Science Program
Department of Materials Science and Engineering
The Pennsylvania State University
University Park, Pennsylvania, PA 16802**

June 1996

**Prepared for the U.S. Department of Energy
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ABSTRACT

Coal liquefaction may involve 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 effects of dispersed Mo catalysts and H₂O addition on hydrogenation and C-C bond hydrocracking of 4-(1-naphthylmethyl)bibenzyl, abbreviated as NMBB.

Recent research in this laboratory has demonstrated a strong synergistic effect between a dispersed Mo sulfide catalyst and water in low-severity coal liquefaction reaction. This finding prompted us to examine the effects of dispersed Mo catalysts and H₂O addition on hydrogenation and C-C bond hydrocracking of 4-(1-naphthylmethyl)bibenzyl, NMBB. Batch studies in microautoclave reactors at 350 and 400°C for 30 min (initial cold H₂ pressure of 6.9 MPa) revealed that active catalysts can be generated in situ from either ammonium tetrathiomolybdate (ATTM) or Mo(CO)₆ under the reaction conditions (350 or 400°C, 30 min), with the main catalysis of the latter for NMBB hydrogenation, but the former for C-C bond cleavage. Water may have strong promoting effect on NMBB conversion in catalytic runs, depending on the conditions. At 350 °C a 50 % increase in NMBB conversion was observed upon H₂O addition to the run using ATTM (1 wt % Mo) as catalyst. However, at 400 °C no major difference in conversion or product distribution was found. Runs of NMBB at 350°C using Mo(CO)₆ lead to tetrahydro-NMBB-derivatives and few cleavage products. Water added to Mo(CO)₆ suppressed hydrogenation. The combination of Mo(CO)₆ and S lead to almost complete conversion of NMBB. A run with Mo(CO)₆/S/H₂O gave similar results. It appears that water can increase NMBB conversion with ATTM at 350 °C but decreases conversion for runs at 400 °C.

Also contained in this report is mechanistic discussion for hydrocracking and hydrogenation of NMBB.

Technical Progress

Effects of Dispersed Mo Catalysts and H₂O Addition on Hydrogenation and Hydrocracking of 4-(1-Naphthylmethyl)bibenzyl

INTRODUCTION

Since Bergius (1) invented coal liquefaction process early in this century, numerous studies have been conducted to make the process more efficient (2,3). It has been demonstrated (2,3) that highly dispersed catalysts can be effective for hydrogenating coal with molecular hydrogen without relying upon a donor solvent. One way to achieve better dispersion is the use of water-soluble inorganic catalyst precursors or oil-soluble organometallic precursors which produce in situ finely dispersed active catalyst particles at elevated temperatures (2-4). Greater catalyst surface area increases the yield of products, due to greater hydrogen activation by augmented reactive catalyst sites. Suitable dispersed catalytic systems contain Mo, Co, Ni, Fe, or their combinations (2,4), either as inorganic complexes, or organometallic species in a concentration of 1 wt % or lower. Good solubility of catalyst precursors may lead to better catalyst dispersion and greater effectiveness for liquefaction reactions (5). The beneficial effect of S on conversion has been demonstrated (6) for a variety of transition metal-based catalysts.

Recent research in this laboratory (7) has demonstrated a strong synergistic effect between a Mo sulfide catalyst and water in low severity coal liquefaction reactions. This finding seems to be contrary to conventional wisdom. Under normal liquefaction conditions, water deactivates Mo-based catalysts (8). In order to help understand the mechanism of water promoted liquefaction reactions, we also examined the effect of water on the catalytic reactions of the model compound NMBB which represents a simplified model of coal.

In this quarterly we report on hydrogenation and hydrocracking of 4-(1-naphthylmethyl)bibenzyl, abbreviated as NMBB (Scheme I), over different Mo-based metal catalyst precursors. The effects of Mo-based catalyst precursors on conversion and product selectivity, as well as the influence of the sulfur and water addition and reaction temperature on the product distribution will be discussed.

Scheme I. Potential cleavage sites in 4-(1-naphthylmethyl)bibenzyl.

EXPERIMENTAL SECTION

Preparation of Catalyst Precursors

Sulfur and ammonium tetrathiomolybdate (ATTM) were purchased from Aldrich, Mo(CO)_6 from Alfa and the model compound NMBB from TCI America. NMBB is also called 1-(4-(2-phenylethyl)benzyl)naphthalene, and is described with this name in TCI News, Summer 1992, No. 4. GC-MS confirmed sufficient purity of NMBB (> 99 %) and it was used without further purification.

Model Compound Reactions

A reactor with a capacity of 33 mL was loaded with ca. 0.25 g NMBB, 1 wt % catalyst precursor (1 wt % Mo based on NMBB) and 0.14 g solvent (tridecane). When water was added, the molar ratio of H_2O to NMBB was 10, corresponding to a wt ratio of H_2O /NMBB of 0.56. The reactor was purged three times with H_2 and then pressurized with 6.9 MPa H_2 at room temperature for all experiments. A preheated fluidized sand bath was used as the heating source and the horizontal tubing bomb reactor was vertically agitated to provide mixing (about 240 strokes/min). After the reaction the hot tubing bomb was quenched in cold water. The liquid

contents were washed with 15 ml CHCl_3 through a low speed filter paper for qualitative and quantitative GC analysis of the filtrate. All runs were carried out at least twice to confirm reproducibility. When sulfur was added, the atomic ratio of S:Mo was 4:1.

The products were identified by GC-MS using a Hewlett-Packard 5890 II GC coupled with a HP 5971A mass-selective detector operating at electron impact mode (EI, 70 eV). The column used for GC-MS was a J&W DB-17 column; 30-m X 0.25-mm, coated with 50 % phenyl 50 % methylpolysiloxane with a coating film thickness of 0.25 μm . For quantification, a HP 5890 II GC with flame ionization detector and the same type of column (DB-17) was used. Both GC and GC-MS were temperature programmed from 40 to 280 $^{\circ}\text{C}$ at a heating rate of 4 $^{\circ}\text{C}/\text{min}$ and a final time of 15 min. The response factors for 10 of the products were determined using pure compounds. More experimental details may be found elsewhere (9).

RESULTS AND DISCUSSION

NMBB Reaction at 350 $^{\circ}\text{C}$

Table 1 shows the results of non-catalytic runs of NMBB in tubing bomb microautoclaves at 300-400 $^{\circ}\text{C}$. NMBB has five possible cleavage (reactive) sites. In the absence of a catalyst, NMBB is essentially inert at 300 $^{\circ}\text{C}$, and shows only very low conversion (4-5%) at 400 $^{\circ}\text{C}$ under H_2 pressure in stainless steel reactors. Farcasiu et al. (10) first carried out model reactions of NMBB in a sealed glass tube in the absence of added catalyst. They reported that there is no reaction of NMBB at 320-375 $^{\circ}\text{C}$ for 1 h, and only 3% conversion at 400 $^{\circ}\text{C}$ for 1 h. Our results for non-catalytic runs in 316 stainless-steel reactors without glass liner are consistent with those of Farcasiu et al. (10) with sealed glass tube. The usefulness of NMBB for model reactions has been shown by Farcasiu et al. (10) and Walter et al. (10) for testing carbon catalysts and various Fe catalysts.

Effect of Precursor Type and S Addition

Table 2 presents the results of non-catalytic and catalytic runs of NMBB with dispersed catalysts at 350 $^{\circ}\text{C}$. NMBB is essentially inert at 350 $^{\circ}\text{C}$ under H_2 pressure in a non-catalytic run. ATTM showed remarkable catalytic effect on NMBB conversion at 1 wt % Mo loading. The main products are 4-methylbibenzyl (4-MBB) and naphthalene, which were formed from

cleavage of bond **a** in NMBB. It is clear that the molybdenum sulfide in situ generated from ATTM at 350 °C is catalytically active, and can promote the cleavage of C-C bond **a** in NMBB. ATTM decomposition also generates extra sulfur. However, our results in Table 1 shows that adding sulfur alone, or H₂O alone, had little effect on NMBB conversion.

The material in situ generated from Mo(CO)₆ at 350 °C acted as a hydrogenation catalyst. The dominant product with Mo(CO)₆ is tetrahydro-NMBB (TH-NMBB). Sulfur addition to Mo(CO)₆ increased NMBB conversion significantly, from 50.8 to 94.3 %. Adding sulfur also changed the product distribution pattern. The major products with Mo(CO)₆ + S are 4-MBB and naphthalene arising from cleavage of bond **a**. The run with Mo(CO)₆ + S also produced considerable amounts of bibenzyl and methylnaphthalene, probably via cleavage of bond **b** in NMBB.

Table 1. Non-catalytic reactions of NMBB at 300-400 °C under 6.9 Mpa H₂.

Experiment #	36-1	36-2	20-1	20-2	21-1	21-1/2
Temp (°C)	300	300	400	400	400	400
Catalyst	None	None	None	None	None	None
Solvent	None	None	None	None	n-C13	n-C13
NMBB Conv [wt %]	1.0	0.9	4.0	3.4	5.2	4.9
Products [mol %]						
Benzene			2.5	2.0	2.4	2.1
Toluene			1.3	0.6	1.1	0.9
Tetralin			0.8	0.3	2.2	1.1
Naphthalene			1.2	1.6	2.2	3.7
1-Methylnaphthalene		0.1				
Bibenzyl	0.1	0.1				
4-Methylbibenzyl	1.0	0.9	2.1	1.9	3.1	3.4
Naphthyltolylmethane			1.3	1.1	1.0	0.8

Table 2. Effect of S and H₂O on hydrocracking of NMBB at 350 °C.

Experiment #	105	95	107-1/ 109-1	94/96/ 108/110	97	98	100	102
Catalyst Precursors*	S [1.4 wt %]	H ₂ O	ATTM	ATTM+ H ₂ O	Mo(CO) ₆	Mo(CO) ₆ + H ₂ O	Mo(CO) ₆ +S	Mo(CO) ₆ +S+H ₂ O
Products [mol %]								
Tetralin			6.6	8.0	3.5		20.6	13.5
Naphthalene	4.4	2.4	25.6	40.0	1.6	1.5	55.4	58.8
2-MTHN ^a				0.1			1.4	0.8
1-MTHN			0.4	0.6			1.7	1.1
2-Methylnaphthalene				0.16			1.9	1.4
1-Methylnaphthalene			1.7	2.9			5.7	5.8
Bibenzyl	0.2		4.7	6.5	0.5		21.2	15.8
4-Methylbibenzyl	3.7	1.9	33.2	50.2	3.8	1.1	74	71.1
TH-NMBB		1.6	5.8	5.3	45.5		2.1	3.1
Conversion [wt %]	4.1	3.7	42.4	60.0	50.8	13	94.3	88.2

^aMethyltetrahydronaphthalene. *when S was added, the atomic ratio S:Mo was 4:1.

Figure 1 compares the product distribution for runs at 350 °C. An interesting result was found in the run with Mo(CO)₆ at 350 °C. Most of the total conversion of 50.8 % can be attributed to the formation of TH-NMBB derivatives (45.5 mol %). This finding suggests that under low severity reaction conditions the initial step in hydrocracking of NMBB is the addition of hydrogen. Several TH-NMBB derivatives (MW 326) can be detected in the GC-MS analysis, indicating hydrogenation of different aromatic moieties in the model compound. At elevated temperatures activated Mo(CO)₆ cleaves NMBB completely; no more TH-NMBB derivatives can be detected, as described later.

Figure 1. Effect of S and water on hydrocracking of NMBB.

Effect of H₂O Addition

The addition of H₂O to ATTM enhanced NMBB conversion and increased the yields of 4-MBB and naphthalene. Therefore, the co-use of ATTM and water appears to be beneficial for NMBB hydrocracking at 350 °C. However, adding H₂O to Mo(CO)₆ decreased NMBB conversion to the level close to a non-catalytic run. This indicates that added H₂O either inhibited the formation of a catalytically active phase or passivated the active sites on the surface of the active phase, or reacted to form some kind of catalytically inactive material. However, adding H₂O to Mo(CO)₆ + S system did not have significant effects on NMBB conversion or product distribution.

It is interesting to note that H₂O addition to the catalytic runs with either ATTM or Mo(CO)₆ + S system did not alter the product distribution pattern, suggesting that the added water did not alter the reaction pathways in these cases.

NMBB Reaction at 400 °C

Table 3 shows the results for non-catalytic and catalytic runs of NMBB at 400 °C. NMBB is not very reactive in a non-catalytic run at 400 °C under H₂ pressure, as its conversion is below 4 %. Sulfur, however, began to show catalytic effect when the temperature is increased from 350 to 400 °C.

Table 3. Effect of Mo-based catalyst precursors on hydrocracking of NMBB at 400 °C.

Experiment #	ES/20/21	78	91	92	106
Catalyst Precursors*	Non-catalytic run	S [1.2 wt %]	ATTM	ATTM+H ₂ O	Mo(CO) ₆
Products [mol %]					
Toluene	1.0	1.4	4.2	3.9	1.5
Tetralin	1.1	0.8	21.8	6.8	49.5
Naphthalene	3.0	24.8	58.1	42.9	10.5
2-MTHN ^a			0.7	0.6	1.2
1-MTHN			1.7	0.5	5.2
2-Methylnaphthalene			1.0	1.5	
1-Methylnaphthalene		1.7	6.8	5.6	0.9
Bibenzyl		2.4	14.5	11.1	12.7
4-Methylbibenzyl	3.3	22.1	77.3	53.1	58.5
TH-NMBB			0		8.5
Conversion [wt %]	3.9	26.1	93.0	63.2	79.6

^aMethyltetrahydronaphthalene, *when S was added, the atomic ratio S:Mo was 4:1.

Both ATTM and Mo(CO)₆ afforded higher conversion of NMBB at 400 °C than the corresponding runs at 350 °C. ATTM alone is a more effective catalyst precursor than Mo(CO)₆ alone, in terms of higher NMBB conversion (93.0 vs. 79.6 %). Addition of water to ATTM in the run at 400 °C, however, had negative impact on NMBB conversion. These results are consistent with those for catalytic hydroliquefaction of coal, where H₂O addition had a strong promoting effect for runs at 350 °C, but inhibiting effect for runs at 400 °C (6).

It appears from our results that water has two opposing effects on NMBB conversion at 350 and 400 °C. Possibility exists that the ratio of water to catalyst is also influential. Farcasiu et al. (10) reported that NMBB bond cleavage at 420-430 °C with various dried iron oxide precursors were different from rehumidified catalysts. Addition of small quantities of water increases, to some extent, the catalytic activity. Completely rehumidified iron oxides showed very low catalytic activity compared to partially hydrated iron oxide. The activity of the system as an acidic catalyst is destroyed by larger amounts of water (longer rehumidification time).

Figure 2 further compares the product distribution for runs at 400 °C. For the runs with ATTM and ATTM+H₂O, 4-MBB and naphthalene are the major products. In the case of Mo(CO)₆, the yield of tetralin is higher than that of naphthalene. Apparently, the activity and selectivity of a dispersed Mo catalyst for NMBB hydrocracking depends on the catalyst precursor type and reaction conditions. Since it is the precursor that was charged into the reactor, an activation into catalyst is involved during the heat up and the subsequent reaction.

Figure 2. Effect of Mo-based catalysts on hydrocracking of NMBB.

It is known (3,5,11) that the S-free catalyst precursors like metal carbonyls require the addition of sulfur for sufficient activity in coal liquefaction; activation of ATTM into the catalytically active species (close in composition to MoS_2) occurs at a temperature of ≥ 325 -350 °C. This temperature range was used in our model reactions. Sulfur addition to Mo(CO)_6 generates MoS_2 after high temperature activation. The resulting product distribution at 350 °C is very similar to runs with ATTM (Table 1). We assume that the active catalytic species is similar to that from ATTM. Unlike ATTM, the organometallic complex Mo(CO)_6 decomposes at much lower temperatures. The active catalyst particles will be readily available under the conditions employed. This may rationalize why the NMBB conversion is higher with Mo(CO)_6 than with ATTM at 350 °C. However, for runs at 400 °C, the NMBB conversions with ATTM and Mo(CO)_6 are similar to each other (8).

With respect to the effect of the catalyst loading level, we have reported some results on NMBB hydrocracking over dispersed catalysts at 2.11 wt % metal loading (8). Decreasing Mo loading level from 2.11 wt % to 1 wt % (this work) did not have negative impacts on NMBB conversion with ATTM, but caused some changes in product distribution from NMBB with Mo(CO)_6 .

Mechanistic Considerations

Scheme II shows the possible reaction pathways leading to the major products observed during reactions of NMBB. It seems that the cleavage of bond **a** or **b** can be rationalized by the attack of hydrogen atom (generated by catalytic dissociation of molecular H_2 on catalyst surface) on the ipso position of the aromatic ring. The relative contribution of these two bonds to NMBB conversion is determined by the stability of the intermediate formed upon ipso-attack of hydrogen atom, and the stability of the resulting radicals. The higher superdelocalizability of the 1-carbon in naphthalene (relative to the carbon in benzene ring) allows for more readily ipso-attack of hydrogen atom on the 1-position in naphthalene ring. This leads to much higher selectivity of bond **a** cleavage. Purely thermal reaction leads to the cleavage of the weakest bond, **d**, in NMBB. Hydrogenation of NMBB can also occur on some catalysts. The main hydrogenation reaction is that of the naphthalene ring. The proposed reaction pathways shown in Scheme II are also consistent with the mechanistic considerations reported by Walter et al. (10). The effects of water addition on catalytic activity are dependent on the type of catalyst precursors. Water addition had a strong promoting effect on NMBB conversion in the runs with

ATTM at 350°C through enhanced bond a cleavage. However, we have not detected oxygenated products in the final product slate in the runs using added water. It is possible that, as one of the working hypothesis, water may enhance catalytic activity by improving the catalyst dispersion (smaller particles) and "cleaning" the catalyst particle surface.

Pathways for Catalytic (1,2,3) and Thermal (4) Reactions

Scheme II. Possible reaction pathways of 4-(1-naphthylmethyl)bibenzyl.

Some discussions in the literature are related to the proposed mechanisms and provide some supporting evidence. Autrey et al. (12) conducted a detailed model compound study on hydrogen transfer pathways on iron-based catalyst. They reported that free radical hydrogen transfer pathways from the catalyst to the alkylarene are responsible for the scission of strong carbon-carbon bonds. According to their report, there are two requisites for the observed

selectivity in bond scission. The first and the most important is the stability of the ipso adduct precursor leading to displacement; the more stable the adduct the more probable bond scission. This explains why $\text{PhCH}_2\text{CH}_2\text{PhCH}_2$ radical displacement > naphthylmethyl radical from NMBB. Second, given "equal" ipso adduct precursor stabilities, e.g., methyldiphenylmethane, the stability of the departing radical determines the selectivity. This explains why benzyl radical > methyl radical in the methylated diphenylmethanes.

Ogata et al. (13) studied the effects of Fe catalysts in hydroconversion of aromatic hydrocarbons, in particular, diarylmethanes. They compared conversions of diphenylmethane (DPM), (1-naphthyl)phenylmethane (NPM), and di(1-naphthyl)methane, over FeS_2 catalyst, and interpreted their results based in part on the superdelocalizability $\text{Sr}(\text{R})$ values of aromatic compounds reported by Futamura et al. (14). A carbon atom in an aromatic ring with larger $\text{Sr}(\text{R})$ value accepts hydrogen atoms more readily. Ogata et al. (13) attributed the observed higher reactivity of DNM than DPM to the following three reasons: 1) the higher hydrogen-accepting ability of the ipso-carbon in DNM than that in DPM due to higher $\text{Sr}(\text{R})$ value of the former; 2) the higher resonance energy (44.4 kcal/mol, from ref. 15) of the resulting 1-naphthylmethyl radical ($1\text{-NapCH}_2^\bullet$) than that (30.6 kcal/mol, from ref. 15) of benzyl radical; and 3) the larger adsorption strength (16) of the naphthalene ring in DNM to the catalyst surface than that of benzene ring in DPM. In the case of NPM, adsorbed H atom can attack the ipso-carbon on either the naphthalene ring or benzene ring. Because of the lower hydrogen-accepting ability of the ipso-carbon in the benzene ring, NPM hydrocracking proceed predominantly via cleavage of the bond between naphthalene ring and methylene linkage, leading to naphthalene and toluene. Ogata et al. (13) attributed the lower reactivity of NPM than DNM to the smaller resonance stability of the resulting $\text{PhCH}_2^\bullet$ radical.

The same group (17) also reported that metallic Fe catalyst accelerated the hydrogenation of aromatic rings, especially bicyclic rings, more than that of monocyclic rings. On the other hand, FeS_2 catalyst, which is converted to pyrrhotite Fe_{1-x}S under reaction conditions, promoted $\text{C}_{\text{ar}}\text{-C}_{\text{alk}}$ bond cleavage of diarylmethanes only, and also promoted the hydrogenation of diarylethanes and diarylpropanes. Based on these results, Ogata et al. (17) concluded that C-C bond cleavage of diarylalkanes is related to the hydrogen-accepting ability, C-C bond dissociation energy, and resonance energy of the species after C-C bond scission.

CONCLUSIONS

Dispersed fine particles in situ generated from either water-soluble precursors such as ATTM or oil-soluble precursors such as $\text{Mo}(\text{CO})_6$, can be effective Mo catalysts for promoting the cleavage of certain C-C bonds such as bond **a** in NMBB at 350-400 °C. When the sulfur-free precursor is used, adding sulfur helps to improve catalytic activity, particularly hydrocracking activity. When ATTM is used at low temperature (350 °C), adding water seems to be beneficial in improving NMBB conversion.

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