MODEL HYDROCRACKING REACTIONS OVER MONOMETALLIC AND BIMETALLIC DISPERSED CATALYSTS.

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Coal liquefaction involves cleavage of methylene and dimethylene bridges connecting polycyclic aromatic units. The selected compound for model coal liquefaction reactions is 4-(1-naphthylmethyl)bibenzyl (NMBB). This work describes the synthesis and screening of several hetero- and homometallic complexes as precursors of dispersed catalysts for hydrocracking of NMBB. Experiments were carried out at 400 °C for 30 min under 6.9 MPa H_2 pressure. $(NH_4)_2MoS_4$ and $MoCl_3$ converted NMBB predominately into naphthalene and 4-methylbibenzyl. Small amounts of secondary products were formed by hydrogenation and fragmentation of the primary products. Lewis acid-type $MoCl_3$ catalyst gave lower selectivity to the primary products, with relatively larger amounts of methyltetrahydronaphthalene- and methylnaphthalene-derivatives. In contrast, the organometallic catalyst precursors $Cp_2Co_2Mo_2(CO)_2S_4$, $Cp_4Fe_4S_4$ and $(Ph_4P)_2(Ni(MoS_4))$ inflict less fragmentation and less hydrogenation of primary cleavage products. $Cp_2Co_2Mo_2(CO)_2S_4$ converted a substantial amount of starting material even at 350 °C; whereas, a noncatalytic run under the same conditions showed only small conversion. Greater product selectivity can be achieved by means of organometallic precursur and low severity reaction conditions. Inorganic and bimetallic catalyst precursors gave similar conversions. The synergistic effect of heterometallic over homometallic catalyst precursors was demonstrated by Co-Mo and Ni-Mo, which gave far higher conversion than the thiocubane-type catalyst containing four iron atoms. The addition of sulfur to $Mo(CO)_6$ and $Co_2(CO)_8/Mo(CO)_6$ gave higher conversion but reduced the yield of hydrogenation products.

Keywords: Model reactions, hydrocracking, dispersed catalysts, monometallic and bimetallic catalysts.

Introduction

First attempts to liquefy coal were carried out in the beginning of the 20th century by Bergius (1). The process is intricit and involves hundreds of different coal components with various functional groups in interconnected aromatic systems. The complexity of coal liquefaction reactions makes it very difficult to study the reaction mechanisms. Therefore, it is extremely difficult to find optimum reaction conditions for selective bond cleavage. Furthermore, coals from different sources may react differently with different catalysts. We selected therefore the model compound 4-(1-naphthylmethyl)bibenzyl (NMBB), which consists of functionalities that are related to coal structures (2-6). Among these are alkyl groups which interconnect aromatic moieties and different ring systems. Of particular interest to our group was the fact that its reaction can give us information about the features of different catalysts. In a typical hydroliquefaction reaction, coal reacts at temperatures above 400 °C with 7 MPa H_2 pressure for a period of ca. 30 min to primary liquefaction products. Efficient conversion can only be achieved by transition metal containing catalysts and metal concentrations of 1 wt % or lower. Suitable catalytic systems contain Co, Ni, Mo or its combinations, either as inorganic complexes, or organometallic species. Good solubility of catalyst precursors generally leads to better catalyst dispersion and greater effectiveness for liquefaction reactions (7,8). One way to achieve better dispersion is the use of soluble organometallic precursors which produce in situ finely dispersed active catalyst particles at elevated tempertures. Greater catalyst surface area increases the yield of products dramatically, due to greater hydrogen acitivation by augmented reactive catalyst sites. Hirschon and Wilson (9,10) demonstrated that highly dispersed catalysts from organometallic precursors can be effective for hydrogenating the coal with molecular hydrogen without relying upon a donor solvent .

This paper reports our work on hydrocracking experiments of NMBB over different transition metal catalyst precursors. The effects of inorganic and organometallic (monometallic and bimetallic) catalyst precursors on conversion and product selectivity will be discussed. Also, the influence of the reaction temperature on the product distribution will be investigated.

Experimental Section

Preparation of Catalyst Precursors. The complexes $(Ph_4P)_2(Ni(MoS_4))$ (11) (Ni-Mo) and $Cp_4Fe_4S_4$ (12) (Fe4) were prepared according to the methods described in the literature, based on the procedures of Brunner and Wachter (11) and Schunn, Fritchie and Prewitt (12). The thiocubane cluster $Cp_2Co_2Mo_2(CO)_2S_4$ (CoMo-TC2) was synthesized earlier (13) in our laboratory. Samples were stored at - 25 °C prior to use. All recrystallizations of the homo- and heterometallic cluster compounds were carried out quickly. The crystalline products are stable on exposure to air but decompose slowely in solution. Sulfur and $(NH_4)_2MoS_4$ (ATTM) were purchased from Aldrich, $Mo(CO)_6$, $Co_2(CO)_8$ from Alfa and the model compound MNBB from TCI America. GC-MS confirmed sufficient purity of NMBB (> 99 %) and it was used without further purification.

Model compound reactions. A stainless steel reactor (tubing bomb) with a capacity of 33 ml was loaded with ca. 0.25 g NMBB, 2.11 wt % catalyst precursor and 0.125 g solvent (tridecane). 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 heating source and the reactor agitated via an oscillator by vertical shaking of the horizontal micro reactor (about 240 strokes/min.) After the reaction the hot tubing bomb was quenched in cold water and the gaseous products collected in a gas bag for further analysis. The liquid contents were washed with 15 ml CH_2Cl_2 through a low speed filter paper and stored in small glass bottles for qualitative and quantitative GC analysis. All runs were carried out at least twice to confirm reproducibility.

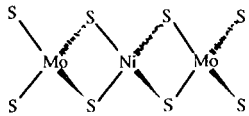
The compounds were identified by capillary gas chromatography-mass spectrometry (GC-MS) using a Hewlett-Packard 5890 II GC coupled with a HP 5971A mass-selective detector operating at electron impact mode (EI, 70 eV). The column used for GC-MS was a J&W DB-17 column; 30-m X 0.25-mm, coated with 100 % phenylmethylpolysiloxane with a coating film thickness of 0.25 µm. For quantification a HP 5890 II capillary GC with a flame ionization detector and the same type of column (DB-17) was used. Both Hewlett-Packard GC and GC-MS were programmed from 40 to 280 °C at a heating rate of 4 °C/min and a final time of 30 min. The response factors of 10 pure compounds were determined. More experimental and analytical details may be found elsewhere (14-17).

Results and Discussion

Hydrocracking of NMBB. Tables 1 and 2 show the results of hydrocracking of the model compound NMBB over different catalyst precursors. In the absence of a catalyst, the conversion at 300 °C is only 1 % and increases to about 4 % at 400 °C. The inorganic catalyst precursor ATTM increased the conversion at 350 °C relative to the thermal run by 54 %. A

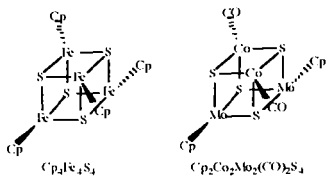
run at 400 °C shows the effect of elevating reaction temperatures. The conversion increased by additional 30 %. Molybdenum trichloride proved to be less effective and gave about 70 % conversion.

Of the catalysts tested, $(Ph_4P)_2(Ni(MoS_4))$ and $Co_2(CO)_8$+S showed the highest conversion (95 %). Ni-Mo consists of a chain like structure with tetrahedral enviroment around nickel and molybdenum (Scheme 1).



Scheme1: Structure of the bimetallic sulfide $[Ph_4P]_2[Ni(MoS_4)_2]$

From the data in Tables 1 and 2 Ni-Mo is apparentely the best precursor and $Cp_4Fe_4S_4$ is the worst among the catalyst precursors tested. A general observation is that the activity of the in situ generated catalysts is smaller at lower temperatures and increases at elevated temperatures. In an attempt to examine the role of bonding between transition metals, we tested the bi-metallic thiocubane-type catalyst $Cp_2Co_2Mo_2(CO)_2S_4$ (Scheme 2), the homometallic cluster $Cp_4Fe_4S_4$ (Scheme 2), and different metal carbonyl combinations which may give (after thermal decomposition) similar catalyst composition as Co-Mo-TC2.

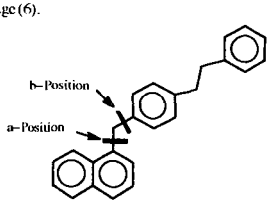


Scheme 2: Structure of the thiocubane-type catalyst precursors $Cp_4Fe_4S_4$, and $Cp_2Co_2Mo_2(CO)_2S_4$.

There are direct metal-metal bonds between Co-Mo, Co-Co and Mo-Mo, besides the sulfur bridges in CoMo-TC2. The question is, do in situ generated catalysts from catalyst precursors which have metal-metal bonds, show different catalytic behaviour. Table 1 shows the superior performance of catalysts containing either Mo, or Co+Mo. Using $Mo(CO)_6$ alone gave similar results as runs with the mixture of two corresponding metal compounds that can also be found in $Cp_2Co_2Mo_2(CO)_2S_4$. Among the testet metal carbonyls, $Co_2(CO)_8$ is less active compared to the thiocubane type catalyst Co-Mo-TC2 and mixed metal carbonyls. A beneficial effect could be observed, when sulfur was added to $Co_2(CO)_8$. NMBB conversion increased dramatically. Addition of sulfur to $Mo(CO)_6$ did not improve the convertibility of NMBB, but added sulfur to $Mo(CO)_6/Co_2(CO)_8$ gave 10 % higher conversion. Work on the advantage of using different metals in a single catalyst reports the synergistic effect of heterogeneous catalysis. The addition of Co or Ni to MoS_2-containing precursors increased their catalytic activity considerably. However, little work has been done on comparison of catalytic effects between mixed metal carbonyls, inorganic- and organometallic heteroatomic precursors. Previous work (18-22) reports mainly the mixture of different transition metal salts.It is known (24-27) that catalyst precursors like metal carbonyls require the addition of sulfur for sufficient activity. The beneficial effect of sulfur addition to hydrogenation reactions was studied on the system molybdenum sulfide and oxide (21). There seems (23) to be consensus that the sulfides of the transition metals are more active in catalytic hydroliquefaction than their oxides. The reason for this remains unclear. Montano and co-workers (28,29) have emphasized the importance of correct stoichiometry between molybdenum oxides and sulfur in high temperature conversion reactions in order to generate catalytically active MoS_2 particles. Temperatures as high as 350 °C are required for this activation process. The analogue transformation of $Fe(CO)_5$ into pyrrhotite ($Fe_{1-x}S$, where $0 \leq x \leq 0.125$) is difficult to perform and iron carbonyls tend to form less reactive iron carbides and oxides (25) during the activation process. This might explain the low activity of our catalyst precursor $Cp_4Fe_4S_4$. The iron catalyst from $Cp_4Fe_4S_4$ would not be active due to the difficulty of forming pyrrhotite. Another reason for the low effectiveness of the iron-cluster in hydrocracking reactions may be that iron appears to function by removing oxygen functionalities whereas Mo catalysts are good hydrogenation catalysts (9). In our previous work, it has been demonstrated that the thiocubane CoMo-TC2 is superior to the mixtures of $Mo(CO)_6$, $Co_2(CO)_8$, and sulfur for liquefaction of a subbituminous coal (13). Comparison of the results in tables 1 and 2 indicates that the thiocubane bimetallic catalysts are not superior to the corresponding mixtures of Co, Mo and sulfur. The rather expensive preparation of the bimetallic catalyst precursors leads to the conclusion that cheaper metal combinations can achieve comparable results. We focused therefore our attention to product selectivity under low severity reaction conditions to study product distribution of NMBB hydrocracking reactions under the influence of homo- and bimetallic catalyst precursors.

Product Distribution

Hydrocracking of NMBB yields three product categories that can be explained by the cleavage of the bonds between the aromatic moieties. The identified products can be classified into hydrocracking, hydrogenation and isomerization products. Those coming from hydrocracking reactions form the major pool of reaction products, followed by hydrogenation and isomerization products. Figure 1 shows the product distribution from catalyst-free reactions. The thermal reaction of NMBB at 300 °C yields only two products, 4-methylbibenzyl (4-MBB) and napththalene (N). Higher temperature (400 °C) gave enhanced conversion and twice as much products. Besides 4-MBB and N, 1-(naphthyl)-4-tolyl methane (NTM) and tetralin can be found as high temperature products. Generally, increased temperature results in lower selectivity. The ratio of major products in our model reactions over thiocubane catalysts (Figure 2) remains similar over a wide temperature range. We can see in Figure 2 more 4-MBB than BB and more naphthalene (N) than tetralin. Several studies, including the present work have shown that NMBB tends to undergo cleavage of bond a connecting the naphthyl group to the remainder of the molecule when subjected to a variety of catalysts under a variety of conditions. Farcasiu et al. suggested a reaction mechanism in which the first stage consists of the formation of a radical cation. The loss of electron density leads to a weakened a-bond which can then be broken relatively easily. This is in contrast to model studies in which phenyl-containing compounds undergo preferably b-cleavage (6).



Scheme 3: Potential Cleavage sites in 4-(1-naphthylmethyl)bibenzyl.

In the work of Penn and Wang (6) radical cations were generated in the mass spectrometer under a variety of conditions which had little impact on the bond cleavage pathway. Preference for b-cleavage was observed. It was explained by resonance stablization of the intermediates formed via bond b cleavage. Both intermediates are resonance stabilized. Thermochemical calculations (30) show that reaction pathway b is 30 kcal/mol lower for both neutral and radical cationic species than pathway a. In contrast, neither of the intermediates resulting from bond a cleavage is stabilized. However, in the presence of a catalyst, the major reaction pathway mainly involves the cleavage of bond a (Scheme 3). These studies indicate that a new decomposition pathway mechanism must be

developed to explain the results of bond cleavage involving model reactions on NMBB. The product distribution is different over metal carbonyls (Figure 3). The main reaction product is 4-MBB, but the ratio of tetralin/naphthalene depends on the addition of sulfur. Sulfur-free metal carbonyl precursors are relatively better hydrogenating catalysts than sulfur containing metal carbonyls and their combinations. This becomes more apparent in the case of Co+Mo and Co+Mo+S. Sulfur enhances the formation of naphthalene and surpresses the generation of tetralin. In order to get more information about the influence of sulfur on hydrogenation reaction, we carried out experiments with tetralin in tridecane as solvent, with and without added sulfur. A sulfur-free run showed only a negligible amount of naphthalene (naphthalene/tetralin ration ≈ 0), but the addition of sulfur lead to a substantially higher naphthalene-to-tetralin ratio (0.08).

Products found in hydrocracking of NMBB over the inorganic catalyst precursor (Figure 4) at 400 °C are similar to those found in runs with organometallic precursors. Unlike all other catalysts, the lewis-acid-type complex $MoCl_3$ gave a different product distribution. $MoCl_3$ is the only catalyst that cleaved both bond a and b in NMBB with about equal probability. The aggressiveness of $MoCl_3$ as catalyst precursor is also demonstrated by a relatively larger percentage of isomerization products. The general observation is that low serverity reaction conditions benefit higher selectivity. At 350 °C ATTM gives a considerable amount of hydrogenation and isomerization products, whereas the organometallic complex CoMo-TC2 yields only products, coming from hydrocracking and hydrogenation reactions. The latter category of compounds can not be found in a reaction involving $Cp_2Co_2Mo_2(CO)_2S_4$ at 300 °C. Higher product selectivity can also be found in experiments with Fe4. This relatively inreactive precursor yields at 400 °C mainly hydrocracking products.

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Table 1. Hydrocracking of NMBB over dispersed metal carbonyls and mixed metal carbonyl with and without added sulfur at 400 °C

Reaction temperature (°C)	300	400	400	400	400	400	400	400
Catalyst Precursor	None	None	$Mo(CO)_6$	$Mo(CO)_6$+ S	$Mo(CO)_6$+ $Co_2(CO)_8$	$Mo(CO)_6$+ $Co_2(CO)_8$ +S	$Co_2(CO)_8$	$Co_2(CO)_8$ +S
Products [wt %]								
Cyclohexane							1.1	2.1
Bezene		0.6	0.2	0.7	0.7	0.7		
Toluene		0.3	1.4	0.5	0.4	0.1	0.7	0.8
p-Xylene			0.7	0.2	0.1		0.3	
Tetralin		0.2	17.3	15.1	21.0	11.7	6.8	5.3
Naphthalene	0.4	0.6	13.8	15.3	5.1	19.2	5.4	28.0
2-MTHN			0.8	0.9	0.6	0.8		0.2
1-MTHN			1.8	1.2	2.4	0.9	1.0	0.5
2-MN			0.5	0.4	0.4	0.5		1.2
1-MN			1.7	1.6	0.5	2.0	0.4	3.0
Bibenzyl			7.7	10.5	6.3	10.3	1.0	9.9
2-MBB			0.4					
4-MBB	0.6	1.3	39.8	38.6	38.3	40.7	14.0	44.8
1-NB							0.4	
NTM		0.9						
THNMBB							6.6	
Other-THNMBB							7.9	
Conversion [wt %]	1.0	3.9	86.1	85	75.8	86.9	45.6	95.8

[a] Reactor residence time in preheated sand bath 30 min. [b] wt % based on the initial weight of NMBB feed.

Table 2: Effect of inorganic and thiocubane-type precursors on hydrocracking reactions[a] of NMBB at 300-400 °C

Reaction temperature (°C)	350[a]	400[a]	400[a]	400[a]	400[a]	300[a]	350[a]	400[a]	400[b]
Catalyst Precursor	ATTM	ATTM	$MoCl_3$	Ni-Mo	Fe4	Co-Mo	Co-Mo	Co-Mo	Co-Mo
Products [wt %]									
Benzene		0.7	0.6	4.9	0.6			0.5	0.6
Toluene		0.1	1.3	1.0				0.6	0.9
p-Xylene			0.3	0.5			0.3		0.4
Tetralin	6.5	14.2	4.5	8.5		0.5	1.6	6.7	9.4
Naphthalene	14.3	16.9	20.9	23.6	4.3	4.0	11.0	24.4	23.2
2-MTHN	0.2			0.4					
1-MTHN	0.8	1.2	0.4	0.8			0.1	0.5	0.6
2-MN	0.1			0.7					
1-MN	1.5	1.7	2.7	2.7			0.6	2.0	2.2
Bibenzyl	3.4	6.3	19.2	6.9	0.3	0.5	1.7	4.7	6.0
2-MBB			3.7	0.2					
4-MBB	28.9	45.1	16.4	44.5	6.5	6.8	18.2	40.9	44.5
Conversion [wt %]	55.7	86.2	70.0	94.7	11.7	11.8	33.5	80.3	87.8

[a] Reactor residence time in preheated sand bath: 30 min. [b] 60 min.

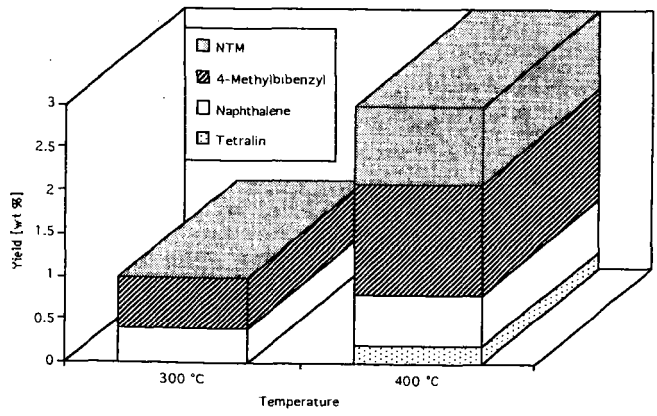

Figure 1: Yields of products excluding gases for non-catalytic thermal hydrocracking of NMBB at 300-400 °C.

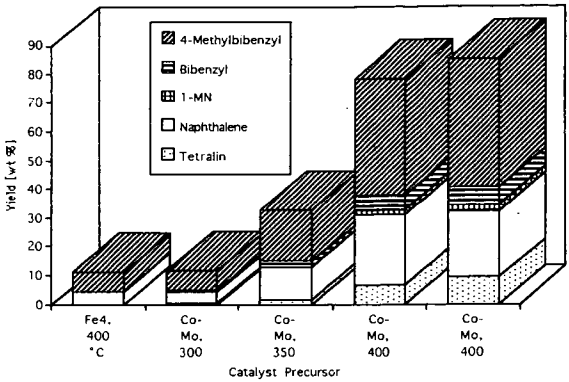

Figure 2: Catalytic activity of thiocubane-type catalysts in the temperature range of 300-400 °C for 30-60 min.

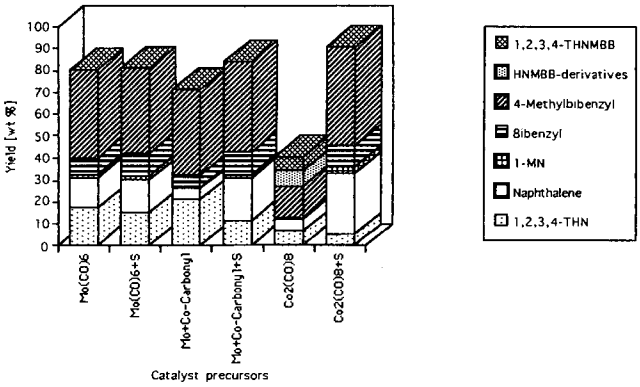

Figure 3. Catalytic activity of mixed metal carbonyls and the mixture plus added sulfur on hydrocracking of NMBB.

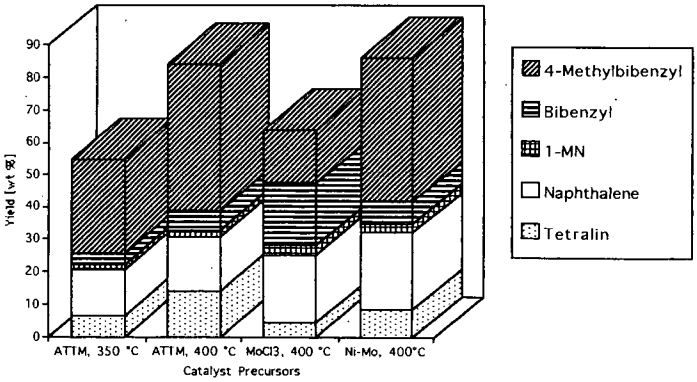

Figure 4: Effect of temperature on hydrocracking of NMBB using inorganic catalyst precursors at 350-400 °C for 30 min.