

INFLUENCE OF SULFUR ADDITION AND S-INDUCED WALL CATALYTIC EFFECTS ON C-C BOND CLEAVAGE AND AROMATICS HYDROGENATION

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Catalytic hydrocracking of 4-(1-naphthylmethyl)biphenyl, designated as NMBB, predominantly yielded naphthalene and 4-methylbiphenyl. Sulfur addition to most catalyst precursors lead to substantially higher catalyst activity and subsequently higher conversion. NMBB was also treated with sulfur alone in the absence of catalysts in concentrations of 1.2 to 3.4 wt, corresponding to conditions present in catalytic runs with added sulfur to precursors. It was found that increasing sulfur concentrations lead to higher NMBB conversion. Furthermore, sulfur had a permanent influence on the reactor walls. It reacted with the transition metals in the stainless steel to form a microscopic black iron sulfide layer on the surface, which could not be removed mechanically. The "non-catalytic" runs which were done after experiments with added sulfur yielded higher conversions than normal runs done in new reactors. This "wall catalytic effect" can be reduced by treating sulfided reactors with hydrochloric acid for a short period of time and subsequent immersing into a base bath overnight. These results demonstrate the significant influence of sulfur addition and S-induced residual wall-effect on C-C bond cleavage and hydrogenation of aromatics in batch reactors.

Keywords: Model reactions, hydrocracking, dispersed catalysts, wall-effect.

INTRODUCTION

Since the early 90's, modern coal liquefaction has reached a point where only minor improvements to the process have been made (1). Sophisticated catalysts have been developed to increase efficiency. Much work still needs to be done in order to fully understand the mechanism on a molecular level, which in turn might lead to an optimized liquefaction process. Model compounds, like NMBB serve as excellent examples of a simplified coal model. Recent work (2,3) examined the effect of various catalysts on hydrocracking of this model compound. It turned out that certain precursors, such as Mo-based and bimetallic systems, show very high activity which can generally be increased by sulfur addition. This finding stimulated our interest to study the influence of S in model compound hydrocracking reactions.

We selected for comparison organometallic compounds and inorganic complexes. Good solubility of catalyst precursors in the liquefaction media generally leads to better catalyst dispersion and greater effectiveness for liquefaction reactions (4). One way to achieve better dispersion is by using soluble organometallic precursors. Ligand loss at elevated temperatures results in an in situ preparation of finely dispersed active catalyst particles. Hirschon and Wilson (5) demonstrated that highly dispersed catalysts from organometallic precursors can be effective for hydrogenating the coal with molecular hydrogen without relying upon a donor solvent. Thus the following work describes our efforts to investigate the influence of dispersed catalyst precursors and sulfur on hydrocracking of NMBB.

EXPERIMENTAL SECTION

Catalyst Precursors

A sample of superfine iron oxide was graciously provided by Mach I Inc. in Pennsylvania. NMBB and sulfur was purchased from TCI America. GC-MS confirmed sufficient purity of NMBB (> 99 %) and it was used without further purification.

Model compound reactions

Runs with NMBB were carried out in 33 mL stainless steel reactors (tubing bomb) at 400 °C for 30 min. In a typical run, a reactor was loaded with ca. 0.25 g NMBB, 2.11 wt % catalyst precursor and 0.14 g solvent (tridecane). The reactor was purged three times with H₂ and then pressurized with 6.9 MPa H₂ 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 and the gaseous products collected in a gas bag for further analysis. The liquid contents were washed with 15 ml CH₂Cl₂ 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.

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 °C at a heating rate of 4 °C/min and a final holding time of 15 min. The response factors for 10 of the products were determined using pure compounds. More experimental details may be found elsewhere (2).

RESULTS AND DISCUSSION

Hydrocracking of NMBB

Initial tests using superfine iron oxide (SFIO), a commercially available sample with a high surface area (250 m²/g), yielded only moderate conversion (27.1 %), even at elevated temperatures (400 °C). The beneficial effect of sulfur addition could once more be demonstrated. Sulfur added to SFIO led to a considerable increase in conversion (78.2 %). A series of experiments was carried out to determine the impact of sulfur concentration on NMBB conversion. It was found that increasing sulfur concentration (starting at 1.2 wt %) led to increasing model compound conversion. As shown in Tables 1 and 2, several catalysts in combination with S were tested to study the impact of sulfur addition for catalytic hydrocracking of NMBB at 400 °C.

Among the tested catalyst precursors (Figure 1), ferrocene is more effective in hydrocracking reactions of NMBB than the inorganic iron complex FeSO₄ x 7 H₂O, which is the least active. However, in the presence of sulfur, FeSO₄ x 7 H₂O shows remarkable activity. The active form from iron sulfate is considered to be pyrrhotite. High temperature activation of ferrous sulfate transforms the inorganic complex in an H₂S atmosphere into an active pyrrhotite phase (6). Adding sulfur to ferrocene had a negative effect on its. This is possibly due to the formation of iron carbide during the initial stage of the catalyst activation. It is known (7) that sulfur addition to iron oxide, or iron pentacarbonyl initiates the transformation into pyrrhotite (Fe_{1-x}S, where 0 ≤ x ≤ 0.125, because of Fe³⁺ impurities). This activation reaction is difficult to perform and iron carbonyls tend to form less reactive iron carbides and oxides during the activation process. Precursor molecules without CO ligands, but cyclopentadienyl groups, are expected to form much more iron carbide. In most reactions, S-presence attains higher conversion than a reaction for the same precursor in a hydrogen atmosphere. Even though molybdenum-based precursors are generally superior to iron-containing complexes, S-addition transforms the latter compound class into a more active phase, probably by providing a better dispersion of iron (8).

It was also found that sulfur had a permanent effect on the stainless steel reactor walls. Even new reactors turn black inside after reactions with S, depending on the sulfur concentration. We assume that added S reacts with iron on the surface of the reactor walls to form FeS. This black FeS layer can not be removed mechanically, and is not removed by base (KOH/i-Propanol/H₂O) for an extended period of time (1 - 3 days). Further experiments of sulfided reactors with NMBB alone gave dramatically higher conversion than identical thermal runs in new reactors. This so called "wall effect" can be reduced by immersing sulfided tubing bomb reactors in a 6 N HCl bath for 5 min. Subsequent treatment of the same reactor in base bath brings "background activity" down by more than 50 %. However, repeated acid washing leaches out steel components and weakens the steel. Furthermore, the surface characteristics of so treated reactors are changed permanently.

The influence of remaining sulfur in the tubing bomb reactors was also investigated. The question arises whether sulfur itself, of sulfided reactor walls are responsible for NMBB cleavage. To clarify this problem, we washed sulfided reactors subsequently with chloroform and ethanol to remove material trapped in the upper part of the tubing bomb reactors. Experiments after this treatment revealed no difference compared to runs without washing the reactor. Therefore, the "residual" catalytic effect seems to be due mainly to the formation of a sulfided layer on the reactor wall. Treatment of tubing bomb reactors with hydrochloric acid partially removes unwanted FeS particles but does not restore the original low activity of a new reactor. More work still needs to be done to understand the influence of sulfur on coal liquefaction experiments. Coal is going to be studied too, because of varied sulfur concentrations which can activate S-free precursors and change their activity substantially.

PRODUCT DISTRIBUTION

The following compounds can be found as main products: tetralin, naphthalene, bibenzyl and 4-MBB. 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. Hydrocracking of NMBB yields three product categories from cleavage of the bonds between the aromatic moieties. Figure 1 and 2 show the product distribution from catalytic hydrocracking experiments of NMBB. All iron-containing catalyst precursors give a ratio of main products similar to each other. It is apparent that ferrous catalysts cleave NMBB preferably in position at the C-C bond α to the naphthyl ring. Increasing conversion leads in most experiments to a proportional increase in the yields of major products. When added in larger amounts (3.4 vs. 1.2 wt %), S not only increased NMBB conversion, but also altered product distribution (Table 2).

Several studies, including the present work, have shown that NMBB tends to undergo cleavage of the C-C bond connecting the naphthyl group to the remainder of the molecule when subjected to a variety of catalytic reactions under a variety of conditions. Farcasiu et al. (3) 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 α-bond which can then be broken relatively easily. This is in contrast to model studies in which phenyl-containing compounds prefer β-cleavage (9). In the work of Penn and Wang (9) radical cations were generated in the mass spectrometer under a variety of conditions but had little impact on the bond cleavage pathway. Preference for β-cleavage was observed. Which was explained by resonance stabilization of the intermediates. Both intermediates are resonance stabilized. Thermochemical calculations (10) show that reaction pathway β is 30 kcal/mol lower for both neutral and radical cationic species than pathway α. In contrast, neither of the intermediates resulting from bond α cleavage are stabilized. However, in the presence of a catalyst, the major reaction pathway mainly involves the cleavage of bond α.

These studies indicate that a new decomposition pathway mechanism must be developed to explain the results of bond cleavage involving model reactions on NMBB.

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REFERENCES

1. Mochida, I. and Sakanishi, K. *Advances in Catalysis*, **40**, 1994, 39-85.
2. a) Schmidt, E. and Song, C. *Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem.*, **35**, 1994 733-737.
b) Song, C.; Schmidt, E. and Schobert, H. H. *DOE Coal Liquefaction and Gas Conversion, Contractors' Review Meeting, Pittsburgh*, (September 7-8, 1994), 593-604.
3. a) Farcasiu, M.; Smith, C. *Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem.*, **1990**, **35**, 404-13.
b) Farcasiu, M.; Smith, C. *Fuel Processing Technology*, **1991**, **29**, 199-208.
c) Farcasiu, M.; Smith, C. and Ladner, E. P. *Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem.*, **1991**, **36**, 1869-77.
4. Artok, L.; Davis, A.; Mitchell, G. D.; Schobert, H. H. and Schobert, H. H. *Energy Fuels*, **1993**, **7**, 67-77.
5. a) Hirschon, A. S.; Wilson Jr, R. B. *Coal Science II, ACS Sym. Ser.*, **1991**, 273-83.
b) Hirschon, A. S.; Wilson Jr, R. B. *Fuel*, **1992**, **71**, 1025-31.
6. Artok, L.; Schobert, H. H.; Davis, A. *Fuel Process Technol.*, in press.
7. a) Herrick, D.; Tierney, J.; Wender, I.; Huffmann, G.P. and Huggins, F.E. *Energy and Fuels*, **4**, 1990, 231.
b) Weller, S. *Energy Fuels*, **1994**, **8**, 415-420.
8. Song C.; Schmidt, E. and Schobert, H. H. *8th ICCS, Oviedo Spain*, September 10-15, 1995, submitted.
9. Penn, J. H.; Wang, J.-H. *Energy Fuels*, **1994**, **8**, 421-425.
10. Ades, H. F.; Companion, A. L.; Subbaswamy, K. R. *Prepr. Pap. - Am. Chem. Soc., Div. Fuel Chem.*, **1991**, **36**, 420-4.

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

Catalyst Precursors ^a	Cp ₂ Fe	Cp ₂ Fe + S	FeSO ₄ x 7 H ₂ O	FeSO ₄ x 7 H ₂ O + S	Superfine Fe ₂ O ₃	Superfine Fe ₂ O ₃ + S
Products [mol %]						
Toluene	1.6	1.1		1.3	1.3	1.9
Tetralin	0.4	0.3		0.6	3.0	4.0
Naphthalene	13.8	10.3	4.5	24.0	16.4	64.1
2-Methylnaphthalene						1.4
1-Methylnaphthalene	5.6	0.5		1.5		5.8
Bibenzyl	2.6	0.6	0.6	2.5	1.0	8.9
4-Methylbibenzyl	9.4	7.4	2.6	19.1	17.4	59.6
Conversion [wt %]	15.8	9.6	3.7	23.9	27.1	78.2

^aWhen sulfur was added, the atomic ratio of S:Fe was 1:1.

Table 2: Effect of Sulfur Addition on Hydrocracking Reactions of NMBB at 400 °C.

Catalyst Precursors	None Catalytic	Sulfur [1.2 wt %] ^a	Sulfur [3.4 wt %] ^a	None [sulfided reactor]	None [reactor HCl treated]
Products [mol %]					
Toluene	0.3	1.4	4.9	1.0	1.0
p-Xylene					
Tetralin	0.2	0.8	2.9	0.8	0.4
Naphthalene	0.6	24.8	74.4	19.1	10.8
2-MTHN ^b			0.4		
2-Methylnaphthalene			7.8		
1-Methylnaphthalene		1.7	9.5	0.8	0.7
Benzyl naphthalene	0.9				
Bibenzyl		2.4	42.5	1.0	1.2
4-Methylbibenzyl	1.3	22.1	32.3	18.3	9.7
Conversion [wt %]	3.9	26.1	82.5	23.0	11.6

^aBased on NMBB, ^bmethyltetrahydronaphthalene.

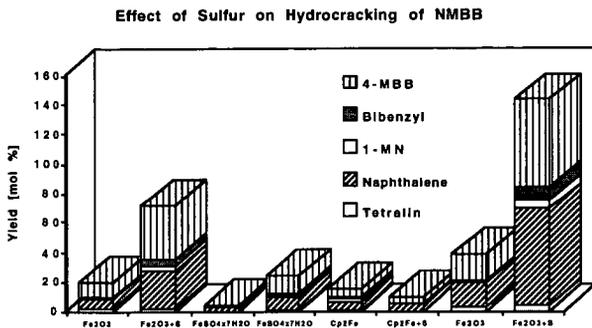


Figure 1: Effect of catalytic hydrocracking of NMBB at 400 ° for 30 min.

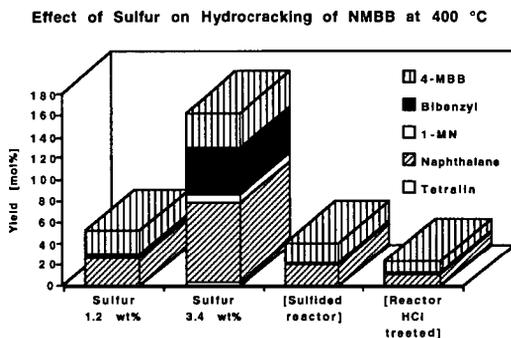


Figure 2: Effect of sulfur on NMBB hydrocracking product distribution at 400 °C for 30 min.

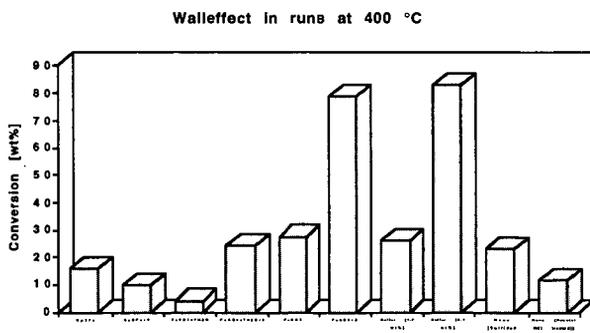


Figure 3: Effect of sulfur on NMBB conversion at 400 °C for 30 min.