

## Hydrogen Sulfide Catalysis of Low Rank Coal Liquefaction

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Research in coal liquefaction catalysis has centered on inexpensive or disposable heterogeneous catalysts, usually naturally occurring minerals consisting of a metallic sulfide such as pyrite, or heterogeneous recoverable catalysts consisting of a transition metal on an acid support such as silica or alumina, which is generally presulfided before use. These catalysts have been tested almost exclusively with bituminous coals, with little emphasis addressing LRC's specific properties, such as high reactivity and oxygen functionality, sulfur deficiency, and smaller molecular size. Only recently has it been proposed that in many, if not all, of these systems that the catalytic effect is due largely to the sulfur rather than the metallic species.

For instance, presulfiding metal oxide hydrogenation catalysts has long been known to enhance liquefaction yields. However, the reason(s) for the enhancement is unclear. Tanabe (1) has ascribed the results to a partial conversion of the metal oxides to metal sulfides, affording mixed sulfide-oxides as more active catalysts. However, during hydrogenation in the presence of presulfided catalysts, hydrogen sulfide is evolved in such quantities that special precautions must be observed when venting the gases from such reaction mixtures to prevent toxic H<sub>2</sub>S from escaping (2). Moroni (3,4) claims to have indirect evidence that gaseous H<sub>2</sub>S is not participating in the reductions of coal since added iron oxides which ordinarily trap H<sub>2</sub>S do not lower liquefaction yields. H<sub>2</sub>S can replace OH groups on alcohols (5, 6) and react with CO to form COS + H<sub>2</sub> (7), which has been shown to be beneficial to coal conversion.

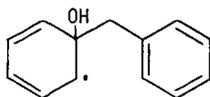
### RESULTS AND DISCUSSION

We have observed that H<sub>2</sub>S is a fine reducing agent for bibenzyl (Table 1), diphenylmethane (Table 2), and diphenyl sulfide (Table 3). The data of Tables 1-3 imply that chemical reactions of H<sub>2</sub>S are of more than one type. First, H<sub>2</sub>S shows hydrocracking ability as evidenced by the conversion of bibenzyl to benzene and toluene. Furthermore it better accomplishes the reduction than pure H<sub>2</sub>, as illustrated by the conversions in Table 1. A similar less dramatic effect is evident in the reactions of diphenylmethane of Table 2.

Second, H<sub>2</sub>S appears to be a hydrogen donor. The remarkable stoichiometry of the bibenzyl reactions of Table 1 requires that hydrogen be transferred from H<sub>2</sub>S to the products as they are forming. Since at 425°C, reaction 1 is known to be operational, it together with the H<sub>2</sub>S hydrogen donation reaction gives H<sub>2</sub> the overall role of a hydrogen transfer agent.

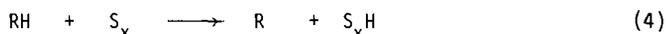
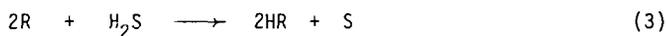
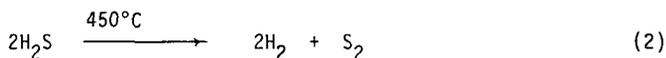


Third, H<sub>2</sub>S can form aromatic-sulfur bonds implying sulfur can attack aromatic rings, cf. Table 2. When H<sub>2</sub>S is reacted with diphenylmethane at 425°C, thiophenol forms in equimolar quantities to toluene. An intermediate of type (I) is plausible for this reaction.



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Fourth, although our data does not directly demonstrate the existence of reaction 2, its existence has been documented at liquefaction temperatures (8). A second source of elemental sulfur is reaction 3. Hence, elemental sulfur may have a role in the liquefaction conditions (9). The various forms of elemental sulfur,  $S_x$ , are expected to exhibit hydrogen abstraction ability, cf. reaction 4. This type reaction appears to best account for the ability of sulfur to rapidly demethylate N,N-dimethylaniline in reducing atmospheres at 425°C (10) and dimerize diphenylmethane at 425°C in the presence of sulfur.



The observed reduction capacity of  $H_2S$  can be attributed to its middle range bond dissociation energy of  $H_2S$  (9). The bond dissociation energy of  $H_2$  is greater than that of most CH bonds, whereas those of  $H_2S$  were nearly the same. The appropriate bond dissociation energies are:



Thus, for  $H_2$ , catalysts of some type are needed unless sufficiently high thermal energy can circumvent the endothermic process.

The conversion of diphenylmethane (DPM) into products is probably due to the presence of sulfur in the reaction mixture. Certainly sulfur promotes the conversion of diphenylmethane into products much more rapidly than  $H_2S$  does (Table 4). At 425°C  $H_2S$  causes little conversion of diphenylmethane. The reaction of S with diphenylmethane is rapid (Table 5) and the product distribution changes with time. The presence of  $H_2S$  along with sulfur enhances the formation of toluene and thiophenol and reduces the yield of large molecule products and conversion (Table 6).

#### ACKNOWLEDGEMENT

We are grateful for the financial support of the Department of Energy under contract DE-AB18-78FC02101.

TABLE 1  
REDUCTION OF BIBENZYL WITH HYDROGEN SULFIDE<sup>a</sup>

<u>Reducing gases</u>	<u>PhH</u>	<u>PhCH<sub>3</sub></u>	<u>PhC<sub>2</sub>H<sub>5</sub></u>	<u>Ph<sub>2</sub>CHCH<sub>3</sub></u>	<u>PhCHCHPh</u>	<u>Conversion</u>
H <sub>2</sub> (750 psig), H <sub>2</sub> O	18.1%	21.3%	17.9%	1%	1%	58.3%
H <sub>2</sub> S(40 psig), H <sub>2</sub> O	0.9	31.8	0	7.6	13.6	53.9
H <sub>2</sub> S(80 psig), H <sub>2</sub> O	5.5	68.3	0	0	0	73.8
H <sub>2</sub> S(120 psig), H <sub>2</sub> O	8.5	84.3	0	0	0	92.8
H <sub>2</sub> S(160 psig), H <sub>2</sub> O	7.1	63.9	0	0	0	71.0
H <sub>2</sub> S(200 psig), H <sub>2</sub> O	4.1	68.4	0	0	0	72.5
H <sub>2</sub> S(240 psig), H <sub>2</sub> O	2.9	64.3	0	0	0	67.2
H <sub>2</sub> S(40 psig)	0.4	10.8	0	7.2	17.3	35.7
H <sub>2</sub> (750 psig)	11.0	14.2	14.5	5.1	0	44.8

<sup>a</sup>Weight percent yield; 2.75 g bibenzyl, Ar added to 1500 psig, reactions done in a 250-ml Hastelloy C rocking autoclave apparatus for 2 hours at 425°C. When water was present, 10.8 ml (0.6 mole) was used.

TABLE 2  
REDUCTION OF DIPHENYLMETHANE WITH HYDROGEN SULFIDE<sup>a</sup>

<u>Reducing gases</u>	<u>PhH</u>	<u>PhCH<sub>3</sub></u>	<u>Thiophenol</u>	<u>Conversion</u>
H <sub>2</sub> (750 psig), H <sub>2</sub> O	1.7%	2.7%	0%	4.4%
H <sub>2</sub> S(40 psig), H <sub>2</sub> O	0	0	0	0
H <sub>2</sub> S(80 psig), H <sub>2</sub> O	T	5.5	6.3	11.8
H <sub>2</sub> S(120 psig), H <sub>2</sub> O	T	7.9	5.1	13.0
H <sub>2</sub> S(200 psig), H <sub>2</sub> O	T	7.0	5.9	12.9
H <sub>2</sub> S(240 psig), H <sub>2</sub> O	T	6.6	4.1	10.7

<sup>a</sup>Weight percent yields; 2.75 g diphenylmethane, Ar added to 1500 psig, reactions done in a 250-ml Hastelloy C rocking autoclave apparatus for 2 hours at 425°C. When water was present, 10.8 ml (0.6 mole) was used.

TABLE 3  
CONVERSION OF DIPHENYL SULFIDE WITH HYDROGEN SULFIDE

Conditions <sup>a</sup>	PhH	PhCH <sub>3</sub>	PhSH	PhCO <sub>2</sub> H	Conversion
H <sub>2</sub> , H <sub>2</sub> O	11.1%	-	2.9%	-	14.0%
CO, H <sub>2</sub> O	6.4	0.4%	2.3	7.5%	16.6
H <sub>2</sub> S, H <sub>2</sub> O	0.6	-	23.6	-	24.2
H <sub>2</sub> , H <sub>2</sub> O, H <sub>2</sub> S	10.0	-	15.4	-	25.4
CO, H <sub>2</sub> O, H <sub>2</sub> S	8.0	0.5	13.6	1.4	23.5

<sup>a</sup>All reactions were run for 32 minutes in 12-ml autoclaves at 450°C.

TABLE 4  
THE PYROLYSIS OF DIPHENYLMETHANE WITH S AND H<sub>2</sub>S-S<sup>a</sup>

System	Sulfur <sup>b</sup>	H <sub>2</sub> S-Sulfur <sup>c</sup>
Time, Min	30	30
Conversion, %	49.9	35.8
Benzene	1.1	1.0
Toluene	3.9	8.0
Thiophenol	6.9	9.0
Diphenylsulfide	trace	0.4
Unknown	-	0.7
Dibenzothiophene	-	0.8
Thioxanthene	0.7	2.0
Triphenylmethane	1.3	0.4
9,10-Dihydro-9,10-diphenylanthracene	0.2	trace
Tetraphenylethylene	0.2	-
12,13-Dihydrodinaphthothiophene	1.6	0.4
1',1',1'-Triphenyl-2-phenylethane	0.3	trace
Large molecule products	35.2	25.2

<sup>a</sup>Reaction temperature was 425°C and the yields are reported in moles per 100 mole of diphenylmethane except for the large molecule products which are reported in weight percent.

<sup>b</sup>The molar ratio of sulfur to diphenylmethane was 1 and the reaction was carried out under an initial charge of one atmosphere pressure of argon.

<sup>c</sup>The molar ratios of H<sub>2</sub>S to diphenylmethane to sulfur was 1:2.5:1.

TABLE 5

THE S-INDUCED PRODUCT DISTRIBUTION ON DIPHENYLMETHANE (DPM) WITH TIME<sup>a</sup>

Time, min.	0 <sup>b</sup>	30	60	120
Conversion %	46.9	49.9	48.8	47.5
Benzene	0.4	1.1	1.3	1.8
Toluene	0.6	3.9	4.2	3.3
Thiophenol	3.0	6.9	7.3	5.5
Unknown	1.2	-	-	-
Thiobenzophenone	0.9	-	-	-
Thioxanthene	1.3	0.7	0.9	0.7
Triphenylmethane	0.5	1.3	1.6	1.1
9-Phenylfluorene	0.9	-	-	-
9,10-Hydro-9,10-diphenylanthroene	0.2	0.2	0.3	0.3
Tetraphenylethylene	7.6	0.4	-	-
12,13-Dihydrodnaphthothiophene	1.6	1.6	1.5	1.7
1,1,1,2-Tetraphenylethane	0.2	0.3	-	0.3

<sup>a</sup>The reaction temperature was 425°C. The sulfur to DPM molar ratio was 2:1 were carried out under an initial charge of one atmosphere pressure of argon. The yields are reported in moles per 100 moles of diphenylmethane.

<sup>b</sup>The heat-up time was 2 minutes.

TABLE 6

THE H<sub>2</sub>S/S INDUCED PRODUCT DISTRIBUTION FROM DIPHENYLMETHANE WITH TIME<sup>a</sup>

Time, min	0	15	30	60	120
DPM Conversion, %	7.8	34.3	35.8	32.9	31.5
H <sub>2</sub> S Conversion, %	12.7	21.3	22.9	22.9	22.9
Benzene	-	0.4	1.0	1.1	1.3
Toluene	-	6.7	8.0	6.9	6.7
Thiophenol	-	7.5	9.0	8.6	8.2
Diphenylsulfide	-	trace	0.4	0.2	0.4
Unknown	-	0.7	0.7	0.6	0.6
Dibenzothiophene	-	0.5	0.8	0.7	0.7
Thioxanthene	0.8	1.5	2.0	1.4	1.2
Triphenylmethane	-	0.2	0.4	0.3	0.2
Tetraphenylethylene	0.3	-	-	-	-
12,13-Dihydrodinaphthothiophene	-	trace	0.4	trace	trace
Tetraphenylethane	trace	-	-	-	-
Large molecule products	15.0	16.7	16.0	17.5	18.4

<sup>a</sup>The reaction temperature was 425°C. The molar ratio of sulfur to DPM to H<sub>2</sub>S was 1:1:2.5. The yields are reported in moles per 100 moles of DPM except for the large molecule products which are reported in weight percent.

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