IRON-BASED CATALYSTS, H_2S AND LIQUEFACTION

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INTRODUCTION

One of the most promising advances of the past 50 years of coal liquefaction catalysis is learning of the iron and sulfur synergism. Now with the promotional effects of hydrogen sulfide demonstrated (1) and its mechanism of action being unveiled (2,3), the interaction of hydrogen sulfide with iron needs to be understood for explaining the basis of presulfiding catalysts and for new catalyst design. Presulfiding metal oxide hydrogenation catalysts has long been known to enhance liquefaction yields. However, the chemistry-based reason(s) for the enhancement is unclear. The metal oxides are probably converted to a mixed oxide-sulfide under sulfur-rich conditions. Using differential thermal analysis under high pressure for coal hydrogenation, Takeya (4) rates red mud + S at 297°C as having better catalytic activity than red red mud at 429°C. A combination of iron oxides and sulfur have been used for coal liquefaction effectively (5,6).

In related studies, Beardon and Aldridge have patented the pretreatment of coal with hydrogen sulfide to enhance conversions (7). Gatsis (8) utilized 4 to 8 volume percent hydrogen sulfide (based on hydrogen gas) to enhance the conversion of bituminous coal (Pittsburgh Seam Coal) into a more filterable, higher hydrogen content product using a solvent. The operating conditions in the extraction zone were 250°-500°C and 500 to 5,000 psig with a solvent to coal weight ratio of 0.2 to 10 and a residence time from 30 seconds to 5 hours. If hydrogen is not present in the extraction zone, then it is recommended that the H_2S amount be increased to 40% based upon the amount of coal fed into the extraction zone. Hettinger has shown that hydrogen sulfide causes a significant increase in hydrocracking (9). Goudrian et al. (10) and Satterfield and Model (11) conclude that hydrogen sulfide improved hydroliquefaction of bituminous coals using hydrogen gas and lignites using synthesis gas. Sondreal, Willson and Stenberg (1) have demonstrated the positive effect of H_2S on lignite liquefaction using synthesis gas. The product stream on the continuous flow unit has lower viscosity, lower gas yield and higher distillable oil yield. This enhancement could be due to the interaction of H_2S with the minerals present in coal.

EXPERIMENTAL

Diphenylmethane was purchased (Aldrich) and recrystallized from its ethyl alcohol solution, cooled and the purity of diphenylmethane determined by GC was over 99.9%. Sulfur (Aldrich) and H_2S (Matheson, Coleman and Bell) were used directly without purification. All the reactions were carried out in a 12-ml 316 stainless steel batch microautoclave (12). The heat-up time was at 2 minutes and cool-down time at 0.5 minutes, respectively. The reaction conditions were as follows: temperature, 300-425°C, mainly 425°C; time, 0-120 minutes, not including heat-up and cool-down times; the molar ratio of sulfur reactants are designated in each table. After the autoclave was cooled, the volume or pressure of gas was measured. The liquid products were washed out from the autoclave with ether, and then analyzed by GC. Instruments for identifying the products were GC-MS and ^{1}H-nmr. A gas chromatograph (Varian 2100) used for the separation of liquid products. Separation was effected by a column (0.64 cm x 183 cm) with 3% OV-17 supported on Suplecoport A.

RESULTS AND DISCUSSION

Diphenylmethane was selected as the model compound for these studies to exemplify the chemical reactions of an aromatic ring-aliphatic side chain in coal. Its chemical structure denies aliphatic elimination reactions. The aromatic-methylene-aromatic bonds apparent absence in SRL, SRC and the lower boiling liquids from coal liquefaction does not detract from diphenylmethane's theoretical value nor

prove its absence of its strucural relatives in coals. Its ability to reflect improved conditions for the liquefaction of coals in the ultimate criterion of value as a model compound. Its behavior under liquefaction conditions has already accurately reflected the H_2S enhancement of coal liquefaction.

The thermal stability of diphenylmethane is higher than bibenzyl and diphenylpropane. Diphenylmethane is thought to be one of the most thermally stable coal-related model compounds. This is bourne out by the data on the pyrolysis of diphenylmethane under various reaction conditions as illustrated in Table 1. Diphenylmethane does not decompose in the argon at the temperature of 425°C and reaction time of 60 minutes. Similar results were obtained in the presence of hydrogen sulfide. However, the decomposition of diphenylmethane was enhanced in the presence of either sulfur alone or a mixture of hydrogen sulfide and sulfur. In the pyrolysis reactions of diphenylmethane, sulfur functions as a reactant and 13 products are formed together with a polymer, cf. Table 1. With either elemental sulfur under argon or under H_2S atmospheres for 30 min, the conversions are 49.9 and 35.8%, respectively.

The presence of H_2S during the reaction of diphenylmethane with sulfur influences the product distribution. With H_2S, the yields of the low molecular weight products, toluene and thiophenol, are higher than those of the comparable reaction with S_8 despite the reduction in diphenylmethane conversion, cf. Table 1. The yield of high molecular weight products, classified as "polymer" in Table 1, was reduced which accounts for the difference.

The yields of gaseous and polymeric products increased with temperature and relative concentration of sulfur with little dependence on time, cf. Table 2. The amounts of gas evolved correlated with the yield of polymeric products under these conditions except when the S_8:diphenylmethane ratio was low. The reactions to form both gaseous and polymeric products are rapid and the yields appear to stabilize after 30 minutes.

Table 3 illustrates that diphenylmethane-S_8 product distribution does indeed change before 30 minutes even though the conversion did within experimental error. Tetraphenylethylene was the principal product in the initial stages of the reaction, and it vanished after 60 minutes reaction time. Benzene, toluene and thiophenol yields appear to be the main benefactors of these secondary reactions. Since the formation of tetraphenylethylene occurs largely within the 2-minute heat-up time, its formation is one of the principal primary reactions occurring in the diphenylmethane mixture. Its incomplete conversion into products is possibly due to either the diphenylmethane-S_8 reaction occurring only in the liquid phase at lower temperatures where sulfur-induced radical reactions are known to occur or a change in the chemical nature and reactivity of sulfur occurred with the reaction time.

In addition to tetraphenylethylene, tetraphenylethane and thiobenzophenone were detected at 300° and 350°C and their concentration decreases with increasing temperature. The low boiling products, benzene, toluene and thiophenol are not formed at 300° and 350°C. Therefore these must be categorized as secondary products.

In the hydrogen gas and/or the H_2S gas, the diphenylmethane conversion was about 4%. Benzene and toluene were formed in about equal amounts. On the other hand, the diphenylmethane conversion was enhanced in a H_2-H_2S mixture gas. The diphenylmethane conversion was H_2S concentration dependent, especially at lower H_2S concentrations, and independent of H_2 concentration under the conditions employed in this study. The main products with the H_2-H_2S mixture gas were again benzene and toluene. Several minor products were formed in less than 1% of the weight of diphenylmethane charged.

The results obtained in a presulfided reactor tube showed that the diphenylmethane hydrocracking was promoted in part by the metal sulfide layer formed on the stainless steel reactor wall. The reactor wall was sulfided with H_2S before the introduction of diphenylmethane which results in a black coating being formed on the reactor wall. Since the metal sulfide is being formed as the reaction proceeds in the nonsulfided metal reactor tube, it is difficult to be certain of the percentage, if any, of the hydrocracking which occurs in the gas phase.

With pyrrhotite, H_2 gas causes considerable hydrocracking of diphenylmethane which contrasts with its behavior in the absence of the iron sulfide. Benzene and toluene are the main products with benzene in excess.

The H_2-H_2S gas mixture over pyrrhotite enhanced the diphenylmethane hydrocracking reaction considerably more than H_2 alone did. Moreover, the diphenylmethane conversion in the presence of pyrrhotite was much higher than that in its absence. The effect of pyrrhotite particle size was not important.

Using pyrrhotite, the diphenylmethane conversion increases rectilinearly with increasing hydrogen pressure. A similar effect on conversion occurs when the hydrogen pressure is kept constant and the reaction time increased. As the rigor of the diphenylmethane reaction solution is enhanced by either increasing the hydrogen concentration or the reaction time, the benzene:toluene ratio increases from the value of 1.

The conversion of diphenylmethane is dependent on the H_2S concentration only until slightly more than a 1:1 mole stoichiometry is achieved whether or not pyrrhotite is present. The yields of benzene and toluene are similarly effected. The increasing concentration of H_2S inhibited the formation of products other than benzene and toluene. The amount of pyrrhotite present influences the conversion but not the product distribution. The pyrrhotite loading attained its optimum effect at a weight ratio to diphenylmethane of 0.5.

The thermal hydrocracking of diphenylmethane in the presence of initiating radicals has been suggested to proceed by reactions 1 and 2. In the absence of initiating molecules such as bibenzyl, the slow thermal decomposition reaction of

$$R^{\cdot} + H_2 \rightarrow RH + H^{\cdot} \qquad 1)$$

$$H^{\cdot} + Ph_2CH_2 \rightarrow PhH + PhCH_2^{\cdot} \qquad 2)$$

$$Ph_2CH_2 \rightarrow 2\,Ph^{\cdot} + PhCH_2^{\cdot} \qquad 3)$$

diphenylmethane, reaction 3 and the thermal decomposition data obtained under argon, provides the only source of $R^{\cdot}$ for reaction 1 with the consequence of slow kinetics of the thermal decomposition of diphenylmethane under hydrogen. Another reason for the slow kinetics of the diphenylmethane decomposition under hydrogen is the endothermic character of reaction 1. From bond dissociation data, one can expect this reaction to be endothermic by 0 to +25 kcal/mole depending on the nature of $R^{\cdot}$. The lack of hydrogen pressure dependence with no additives present is probably an artifact attributed to the low level of conversion and obscurred by experimental error.

With hydrogen sulfide and hydrogen present, the conversion and product yields are significantly higher. These results are consistent with reactions 4 and 5 becoming operational in the reaction mixture. The hydrogen sulfide pressure

$$R^{\cdot} + H_2S \rightarrow RH + {}^{\cdot}SH \qquad 4)$$

$${}^{\cdot}SH + H_2 \rightarrow H_2S + H^{\cdot} \qquad 5)$$

dependence is rationalized by reaction 4 and its maximum concentration optimum is controlled by reaction 5 which regenerates H_2S. The reaction sequence 4 and 5 is a thermodynamic stepwise alternative to the highly endothermic reaction 1. Thus, the hydrogen sulfide effect is suggested to take place by replacing reaction 1 with two potentially faster reactions which accomplished the same end result. Reaction 4 is estimated to be endothermic or exothermic by the range of -9 to +16 kcal/mole and 5 endothermic by +9 kcal/mole. Therefore, hydrogen sulfide functions as a H-transfer catalyst in a hydrogen-hydrogen sulfide gas mixture, and this results in an enhanced diphenylmethane hydrocracking reaction.

The significant changes on using pyrrhotite together with hydrogen and hydrogen sulfide is rate enhancement, hydrogen and hydrogen sulfide dependence and increased benzene formation. The rate enhancement can be attributed to a weakening of the SH bonds or outright dissociation of H_2S on the pyrrhotite surface which serves to enhance the rate of reaction 4. The hydrogen pressure dependence with pyrrhotite is attributed to the increased concentration of an active ${}^{\cdot}SH$ and reaction 5 becoming a significant factor in the reaction mixture. Since benzene is formed in higher yields than toluene and toluene is converted in low yield into benzene under these conditions in the absence of pyrrhotite, adsorption of diphenylmethane on the

pyrrhotite surface is indicated and the benzene in excess of a stoichiometric ratio with toluene formed from some adsorbed species.

Two factors were considered in the design of new iron oxide supported catalysts: (a) iron is the principal transition metal to be used based on the cost factor, and (b) the acidity of the support oxide should be varied to determine the optimum acidity. These metal oxides have been screened and the promising results published (3). Since then, we have continued work with these catalysts using sulfur additives and have obtained much more exciting results than those published, cf. Tables 5 and 6.

Diphenylmethane is converted into mainly benzene and toluene when exposed to reducing conditions at liquefaction temperatures such as 425°C (Table 5). When hydrogen is used in the stainless steel reactor with no added catalyst there is no conversion of the starting material. When metal oxide heterogeneous catalysts are added, the starting material is converted into the observed products to varying degrees (Table 6). All three newly designed and synthesized catalysts are active and compare favorably with the commercially available $CoO-MoO_3$. Table 6 gives data which demonstrate the positive effect of sulfiding the catalysts before or during use. The SiO_2- supported catalyst was selected for the present study on the basis of cost effectiveness.

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Table 1 The Pyrolysis of Diphenylmethane with S_8 and H_2S/S_8[a]

Products[b]	S	H_2S/S
Benzene	1.1	1.0
Toluene	3.9	8.0
Thiophenol	6.9	9.0
Diphenyl sulfide	Trace	0.4
Unknown	0.0	0.7
Dibenzothiophene	0.0	0.8
Thioxanthene	0.7	2.0
Triphenylmethane	1.3	0.4
9-Phenylthioxanthene	Trace	Trace
9,10-Dihydro-9,10-diphenylanthracene	0.2	Trace
Tetraphenylethylene	0.2	0.0
12,13-Dihydrodinaphthothiophene	1.6	0.4
1,1,1-Triphenyl-2-phenylethane	0.3	Trace
Polymer	35.2	25.2
Conversion	49.9	35.8

[a]The reactions were done at 425°C for 30 min. at temperature with $H_2S:Ph_2CH_2:S$ ratio of 2.5:1:1. The sulfur reaction was done under an argon atmosphere.
[b]The results are given in mole percent based on the amount of starting material except for the amount of polymer. The latter is given in weight percent of Ph_2CH_2 plus S charged.

Table 2 The Reaction of S_8 with Diphenylmethane

Temp, °C	Time, min	Mole ratio $S:Ph_2CH_2$	Gaseous products, wt%[a]	Polymeric products, wt%[a]
300	30	1	1.0	14.8
350	30	1	2.7	29.8
425	30	1	6.6	35.2
425	60	1	7.0	33.6
425	120	1	6.8	34.0
425	30	0.5	4.6	9.9
425	30	2	18.1	44.2
425	0[b]	1	5.6	24.2

[a]Weight percent of total sulfur plus diphenylmethane charged.
[b]The heat-up time was 2 minutes with an immediate temperature quench.

Table 3 Time Dependence of S_8-Ph_2CH_2 Product Distribution[a]

Products[b]	Time at temperature, min			
	0[c]	30	60	120
Benzene	0.4	1.1	1.3	1.8
Toluene	0.6	3.9	4.2	3.3
Thiophenol	2.0	6.9	7.3	5.5
Unknown	1.2	0	0	0
Thiobenzophenone	0.9	0	0	0
Thioxanthene	1.3	0.7	0.9	0.7
Triphenylmethane	0.5	1.3	1.6	1.1
9-Phenylfluorene	0.9	0	0	0
9,10-Dihydro-9,10-diphenylanthracene	0.2	0.2	0.3	0.3
Tetraphenylethylene	7.6	0.4	0	0
12,13-Dihydrodinaphthothiophene	1.6	1.6	1.5	1.7
1,1,1-Triphenyl-2-phenylethane	0.2	0.3	0	0.3
Conversion	46.9	49.9	48.8	47.5

[a]The reaction temperature was 425°C; the S:Ph_2CH_2 mole ratio was 1; and the reactions were done under an atmosphere of argon.
[b]The results are given in mole percent based on the diphenylmethane charged.
[c]The heat-up time was 2 min with an immediate temperature quench.

Table 4 Diphenylmethane Conversion with S_8-H_2S[a]

Products[b]	Time at temperature, min				
	0[c]	15	30	60	120
Benzene	0	0.4	1.0	1.1	1.3
Toluene	0	6.7	8.0	6.9	6.7
Thiophenol	0	7.5	9.0	8.6	8.2
Diphenyl sulfide	0	Trace	0.4	0.2	0.4
Unknown	0	0.7	0.7	0.6	0.6
Dibenzothiophene	0	0.5	0.8	0.7	0.7
Thioxanthene	0.8	1.5	2.0	1.4	1.2
Triphenylmethane	0	0.2	0.4	0.3	0.2
Tetraphenylethylene	0.3	0	0	0	0
12,13-Dihydrodinaphthothiophene	0	Trace	0.4	Trace	Trace
Polymer	24.4	27.9	25.2	27.6	29.0
Ph_2CH_2 conversion	7.8	34.3	35.8	32.9	31.5

[a]The reaction temperature was 425°C and the H_2S:S:Ph_2CH_2 molar ratios were 2.5:1:1.
[b]The results are given in mole percent based upon the amount of starting material except for the amount of polymer. The latter is given in weight percent of Ph_2CH_2 plus S_8 charged.
[c]The heat-up time was 2 min with an immediate quench.

Table 5. Diphenylmethane Product Distribution Using the Fe_2O_3 - SiO_2 Catalyst[a]

Gases Added / Products	CO H_2O H_2S (P)	H_2 H_2S (P)	H_2 S	H_2[b] (U)	H_2 H_2S (U)
Benzene	1	83	71	43	105
Toluene	1	75	67	21	88
Cyclohexanes	0	3	7	0	5
Others	0	1	2	8	1
Conversion	1	88	81	41	100

P=presulfided
U=unsulfided

[a]The reactions were done in the 12ml rocking autoclaves at 425°C for 1 hr. H_2 (4.9 x 10^{-1} moles), H_2S (3.9 x 10^{-3} moles), and diphenylmethane (3 x 10^{-3} moles) were used. A 10 weight percent load of catalyst was used. The cited data is duplicate results. The presulfiding was done by exposing the catalyst to 250 psi H_2S, 1400 psi H_2 and raising the temperature to 425°C and keeping it there for 1 hr.

[b]The reaction temperatrue was 450°C.

Table 6. The Reaction of Diphenylmethane Using the Tanabe Newly Synthesized Catalysts[a]

	None	Fe_2O_3	Fe_2O_3 on ZrO_2	Fe_2O_3 on TiO_2	Fe_2O_3 on SiO_2	$CoO \cdot MoO_3$
$CO/H_2O/H_2S$	NA	Trace	4	2	Trace	34
H_2/H_2S	NA	30	82	98	100	99
H_2/S	9	30	92	95	81	99
H_2[b]	NA	5	45	16	23	96
$H_2/H_2S/H_2O$	NA	2	3	4	4	26

[a]The reactions were done in the 12ml rocking autoclaves at 425°C for 1 hr. H_2 (4.9 x 10^{-1} moles), H_2S (3.9 x 10^{-3} moles), and diphenylmethane (3 x 10^{-3} moles) were used. A 10 weight percent load of catalyst was used. The cited data is duplicate results. The presulfiding was done by exposing the catalyst to 250 psi H_2S, 1400 psi H_2 and raising the temperature to 425°C and keeping it there for 1 hr.

[b]The catalyst is presulfided for this run.